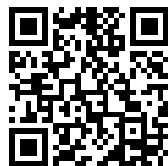

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or quia ex se fila gignunt, nec noster
ust. *Livs. Polit. lib. i. cap. 1. Not.*

TH SERIES.

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CONDUCTED BY

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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster
vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. 1.* Not.

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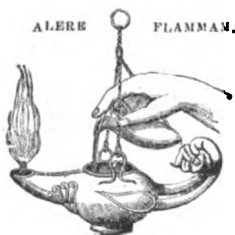
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“Meditationis est perscrutari occulta; contemplationis est admirari
perspicua Admiratio generat quæstionem, quæstio investigationem,
investigatio inventionem.”—*Hugo de S. Victore.*

—“Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condât,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu.”

J. B. Pinelli ad Mazonium.

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[SIXTH SERIES.]

JANUARY 1924.

I. *Notes on Corpuscular Radiation excited by X-Rays.* By C. G. BARKLA, F.R.S., and Miss A. E. M. M. DALLAS, M.A., B.Sc., Carnegie Fellow, University of Edinburgh*.

THE recent important experimental work of M. de Broglie, of Whiddington, and of Shearer on the corpuscular radiation emitted from substances exposed to X-rays, emphasizes the need of further quantitative measurements upon radiation of this type. It will, however, be an advantage to recall the results of energy measurements which have already been made, for these appear to possess a significance which cannot be overlooked in a complete study of the subject. We propose therefore to give a brief account of these earlier experiments which led us to undertake the investigations described later.

The *maximum* velocity of emission of the electrons from metal plates was shown by Cooksey and Innes to be a function only of the penetrating power (or frequency) of the exciting radiation. Later it was assumed that it was given by the relation $\frac{1}{2}mv^2 = hn$: hence the frequency (n), and wave-length of the X-radiation was found. The method was later justified by the sufficiently close agreement with the wave-length determinations made by the interference method.

Accurate measurements show no appreciable variation in the *maximum* velocities of emission from various substances, and it is certain that for these $\frac{1}{2}mv^2$ differs little from hn .

* Communicated by the Authors.

Phil. Mag. S. 6. Vol. 47. No. 277. Jan. 1924.

B

Shortly after the discovery of the characteristic X-radiations, however, Barkla* had observed the large sudden increase in the ionization produced in a gas, and Sadler† the increase in electronic emission from a metal plate when the primary radiation traversing these passed the critical frequency essential to the emission of a characteristic X-radiation in each. One of us later pointed out that the electrons of the corpuscular radiation were emitted in clearly defined groups, each group being associated with a characteristic X-radiation from the substance. Thus a substance traversed by X-rays emits distinct groups of electrons constituting the K, L, M, etc. corpuscular radiations (producing K, L, M, etc. ionizations if the substance is in a gaseous form), associated with the emission of K, L, M, etc. characteristic radiations. The question naturally arose as to whether or not the velocity of emission of an electron from the parent atom depended upon the group of which the electron was a member, that is, upon the particular characteristic radiation with which it was associated.

As the energy of electrons ejected by an X-radiation of frequency n does not range continuously from hn downwards‡, the only alternatives which appear to have any theoretical probability are that the energy of escape from the parent atom is approximately hn , or that it is hn diminished by hn_k , hn_l , hn_m (say), this latter quantity being dependent on the particular group to which the ejected electron belongs. Thus the energy of a K electron—by which we mean an electron emitted in association only with the K characteristic radiation, whatever its origin—might be $h(n-n_k)$ where n_k is the critical absorption frequency in the substance for the K radiations,—or at any rate something near to that.

It is, however, quite a simple matter to decide experimentally between these *if they are the only two alternatives*. Experiments have been undertaken with that purpose, and other experimental results may be shown to furnish evidence on the same point. These experiments have been of two kinds in which the substance used has been in the form of (1) a gas, (2) a solid plate. In the case of gases traversed by X-rays, the energy of corpuscular emission has been measured by the ionization produced by the electrons in

* 'Nature,' April 15, 1909; Camb. Phil. Soc. Proc. May 1909; Phil. Mag. August 1910.

† Phil. Mag. March 1910.

‡ See C. T. R. Wilson's photographs.

the gas itself. Such measurements give the total energy without the necessity for any correction due to absorption. The energy of emission of electrons from plates exposed to X-rays has been measured by the ionization produced in a gas (usually air) just outside the surface. Such measurements, unless they are merely relative, involve a calculation of absorption based on somewhat questionable assumptions, and they give no indication of slowly moving electrons. But a comparison of these measurements both among themselves and with those obtained in experiments on gases lead to important conclusions.

We will first consider the results of experiments upon gases, as these are the more consistent; their interpretation is also less open to question.

GAS EXPERIMENTS.

The first application of ionization experiments to the measurement of the energy of corpuscular radiation was made by Barkla and Philpot*. This led at once to the conclusion that when a beam of X-rays is absorbed in a substance and little energy is re-emitted as characteristic radiation, the energy of the corpuscular radiation is approximately independent of the substance. In other words, the energy of the corpuscular radiation excited by an X-ray beam is proportional to the energy of the X-radiation absorbed whatever the absorbing substance—provided no appreciable amount of energy is re-emitted as fluorescent (characteristic) radiation. The condition may be otherwise expressed as: “provided the frequency (n) of the primary radiation is much greater than that (n_k or n_l) of any characteristic radiation excited in the absorbing substance.” It should be noticed that this was found to be true (with a maximum variation of only about 7 per cent.) for gases containing elements of atomic weight as high as 127 (iodine), and that in some cases the K corpuscular radiation was emitted, in others not. It is tolerably certain, then, that it is perfectly general. On either of the two suggested alternatives—that $E=hn$, or $E=h(n-n_k)$ —this would imply that under these conditions the number of electrons emitted is (approximately) independent of the absorbing substance—which is the form of the conclusion as stated in the original paper.

The interesting question then arose as to the energy

* Phil. Mag. June 1913.

of corpuscular radiation when n is only slightly greater than n_k and the characteristic X-radiation is excited in considerable intensity in the substance traversed by the primary beam. We already had data on this point, for Barkla has found* the sudden increase in ionization in C_2H_5Br when the frequency n of the ionizing radiation passed beyond the critical frequency (n_k) of bromine. The results are shown in Table I., where column 1 gives the ionizing radiations used, column 2 the wave-length of the α_1 constituent of this K radiation, column 3 the observed ionization in C_2H_5Br compared with that in an equal short path in air at the same pressure. With the purpose of obtaining accurate data in the critical region, the experiments were later performed in an entirely different way and with great care†, and the results given in column 4 were obtained. (In the first set the C_2H_5Br was mixed with air; in the later one the C_2H_5Br was pure.) The agreement between the two is quite close and leaves no doubt of the substantial accuracy of the relative ionizations.

TABLE I.

(1)	(2)	(3)	(4)
Radiation used.	Wave-length of $K\alpha_1$ constituents.	Ioniz. coeff. in C_2H_5Br . Ioniz. coeff. in air	As (3).
Fe K radiation	1.932×10^{-8} cm.	x	x
to	to		
Br K radiation	1.035×10^{-8} cm.	x	x
.			
Sr K radiation	$.871 \times 10^{-8}$ cm.	$3.5 \times x$	$3.3 \times x$
Mo „	.710 „	$4.4 \times x$	$4.4 \times x$
Ag „	.562 „	$5.1 \times x$	$5.6 \times x$
Sn „	.487 „	$5.8 \times x$	$6.0(7.9) \times x$
Sb „	.468 „	$5.5 \times x$	
Ce „	.355 „		$6.8(9.5) \times x$

The results show that as the frequency of the radiation passing through C_2H_5Br is increased, the ionization coefficient remains quite normal, being a constant (x) times that in air for instance, until the ionizing radiation has a frequency greater than the critical frequency for Br. Then there is a sudden and large rise in the ionization coefficient. How sudden this is was not shown by these

* Phil. Mag. August 1910.

† Bakerian Lecture 1916, Phil. Trans. 1917.

experiments, but when Sr "K" radiation was used, with wave-lengths about 16 per cent. shorter than the wave-lengths of corresponding radiations from Br, the ionization in the C_2H_5Br had increased to 3.5 times the normal value.

Again, confirmation of these results is obtained by a comparison with Beatty's values obtained for the ionization in SeH_2 and shown in Table II. The corresponding columns 1, 2, and 3 have the same meaning as in Table I.

TABLE II.

(1)	(2)	(3)
Radiation used.	Wave-lengths of $K\alpha_1$ constituents.	Ioniz. coeff. in SeH_2 Ioniz. coeff. in air
Fe K radiation	1.932×10^{-8} cm.	//
to	to	
Se K radiation	1.104×10^{-8} cm.	y
.		
Sr K radiation	$.871 \times 10^{-8}$ cm.	$4.1 \times y$
Mo ..	.710 ..	$6.3 \times y$
Ag ..	.562 ..	$7.7 \times y$
Sn ..	.487 ..	$8.3 \times y$
I ..	.437 ..	$9.5 \times y$

Selenium has a lower, critical frequency than Br; the magnitude of the increase in ionization is, however, almost exactly as found for bromine under corresponding conditions.

Now the critical absorption wave-length in Br is $.916 \text{ \AA.U.}$ according to de Broglie, or $.9179 \text{ \AA.U.}$ according to Duane. We thus see that when the frequency of the ionizing radiation (Sr K radiation) is in the main about 5 per cent. greater, the increase in ionization is 2.5 times the "normal" ionization—i. e., the K ionization is 2.5 times the L, M, N etc. ionizations together.

Considering now the two alternatives mentioned above, if $\frac{1}{2}mv^2 = hn$ and these K electrons thus move with approximately the same velocity as the L, M, and N electrons, there are 2.5 times as many ejected K electrons as ejected L, M, N, etc. electrons. But if the K electrons move with the velocity given by $\frac{1}{2}mv^2 = h(n - n_k)$, then the number of K electrons ejected is more than 30 times as great as the L, M, N electrons together.

Now if the energy of each electron is assumed to be hn , we arrive at the very simple and satisfactory conclusion that one electron is ejected in association with each quantum

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of characteristic radiation*: This relation holds very closely not only when n is just greater than n_k , but also when it is much greater.

On the other hand, on the hypothesis that $\frac{1}{2}mv^2 = h(n - n_k)$ there must be many more, say roughly 10 "K" electrons, for each quantum of K characteristic radiation from bromine; and this number steadily diminishes with an increase in n . If this were the case, we should be led to one of two alternative conclusions:—either that one quantum of characteristic radiation is emitted for only one electron in every ten say, or that the characteristic radiation is not emitted in quanta, but in small fractions of a quantum. All the evidence is against the latter assumption; no one even suggests it. Neither is there any support for the former supposition—that the emission of characteristic radiation is only an occasional accompaniment of the emission of K electrons. That would be contrary to the accepted quantum theory of radiation and to the hypothesis which demands that the energy of ejection shall be $(h\bar{n} - n_k)$.

Briefly, then, if the K electrons are ejected from the atom with the energy hn , there is one electron ejected for from two to one quantum of primary radiation absorbed; there is one electron ejected for each quantum of K characteristic radiation emitted, not only when n is just greater than n_k but when it becomes much greater.

On the other hand, if the energy of ejection be $h(n - n_k)$ these electrons are many times more numerous than the number of quanta of primary radiation absorbed, or than the number of quanta of characteristic K radiation emitted in association with them. Also the magnitude of their excess varies with the frequency n of the primary radiation. This is all contrary to the assumption necessary to explain the energy $h(n - n_k)$ at all!

This, however, does not show that *some* of the K electrons are not emitted with energy $h(n - n_k)$. There might conceivably be the required number of such electrons when n is just greater than n_k , and in addition an approximately equal number of swiftly moving electrons of energy hn . But such an assumption would mean, on this view, that the K group consisted of electrons both from the K level and from other—say L, M, and N levels.

It must be remembered, however, that no K electron is emitted unless $n > n_k$, *i. e.* this condition applies to *all*

* Barkla, Bakerian Lecture 1916.

electrons in the K group; so if some of these electrons are ejected from L, M, or N levels, it must be as a consequence of the ejection of electrons from the K level—that is, they must be ejected from the same atom. In other words, two electrons in the same atom would absorb one quantum of primary radiation, first the K electron, then an L, M, or N electron. This is highly improbable on any theory yet put forward, but is not inconceivable.

The following conclusions, which can hardly be disputed, may be drawn from the ionization experiments considered alone:—

The K ionization is *not* produced simply or even principally by electrons with energy $h(n-n_k)$. The K ionization *may* be produced by electrons with energy hn ,—indeed, if we assume that the K ionization is principally by such electrons, then we find that one quantum of K characteristic radiation is emitted for each electron.

While there is a possibility that many K electrons are emitted with energy $h(n-n_k)$, no suggested theory which takes them into consideration seems capable of explaining the K ionization quantitatively.

PLATE EXPERIMENTS.

The experimental results (published by a number of observers) on the corpuscular emission from plates seem also to indicate unquestionably that the vast majority of the K electrons (*viz.* those electrons emitted in association with K characteristic radiation whatever their origin) have substantially the same velocity as the other (L, M, N, ...) electrons ejected by the same primary radiation.

The evidence is of two kinds: the first based on observations of the *increase* in electronic emission when n exceeds n_k , the second based on measurements of the *total energy* (ionizing power) of the electrons.

The K increase of electronic emission.

SADLER: Thus Sadler* records something like a twenty-fold increase in the energy of corpuscular radiation emitted from a metal plate when the frequency of the primary radiation falling upon it is raised above that necessary to excite the K characteristic radiation. This is shown when Ni radiation (K) falls on Fe and when As radiation falls on Cu. (For wave-lengths see Table III.) Yet the

* Phil. Mag. March 1910.

absorbability of the corpuscular radiation (principally K electrons) is quite normal, following the same law as for the L, M, N electrons ejected from other substances by Ni and As radiations respectively.

TABLE III.
Wave-lengths of K radiations. (Unit= 10^{-8} cm.)
(From Siegbahn.)

	β_2	β_1	α_1	α_2
Fe	1·741	1·753	1·932	1·9366
Co	1·606	1·617	1·786	1·790
Ni	1·484	1·497	1·655	1·659
Cu	1·377	1·389	1·537	1·541
Zn	1·279	1·293	1·432	1·436
As	1·038	1·052	1·173	1·177
Se		·993	1·104	1·109
Br	·914	·929	1·035	1·04
Sr	·767	·779	·871	·876
Mo		·633	·710	·714
Ag	·491	·501	·562	·567
Sb		·432	·487	·490
Sa	·408	·416	·468	·472
Ce		·314	·355	·360

While for certain reasons these results are not altogether satisfactory, they must be very strangely in error if they do not show that the K electrons emerging from the plate move with substantially the same velocity as the L, M and other electrons. On the other hand, the increase in the energy of corpuscular emission observed by Sadler is certainly enormously larger than we have ever obtained from other elements—(see later)—and is difficult to account for on the basis of only an 8-fold increase in absorption. The absolute energy measurement, too, does not agree with that of other observers.

Bragg: Again, though W. H. Bragg did not undertake a systematic investigation of the point, a fragment of the results of experiments by Bragg and Porter* indicates the sudden large increase in the corpuscular emission from a plate of zinc when the primary radiation was only just sufficiently penetrating to excite the K characteristic

* Proc. Roy. Soc. 1911.

radiation. Thus when Zn radiation fell upon Zn, the corpuscular emission was only $\cdot 33$ of that from Fe exposed to the same radiation; but when As radiation was used, the emission from Zn became $1\cdot 28$ times as great as that from Fe. That is, the corpuscular emission increased in the ratio $1:3\cdot 84$ when the K characteristic radiation was excited in Zn.

Or comparing with the emission of electrons from Ni, the sudden increase in the emission of electrons from Zn is given by the ratio $1:3\cdot 80$.

This meant that the K electrons emerging from the Zn plate have nearly three times ($2\cdot 8$) the energy of the L, M, N electrons, when the exciting radiation (As "K" radiation) has a frequency only about 20 per cent. greater than the frequency of the corresponding radiation from Zn, and the bulk of the exciting radiations has a frequency only about 10 per cent. greater than the critical absorption-frequency for Zn.

The increase is very much smaller than that recorded by Sadler, but it has every appearance of being of the right order of magnitude. The observations appear more consistent than Sadler's, and this isolated result agrees very closely with the sudden increase previously observed by us in the ionization in ethyl bromide, already referred to, when the frequency of the ionizing radiation was correspondingly greater than the characteristic frequency for bromine.

BEATTY: Further, though Beatty* does not show the variation in the energy of emission of electrons from a plate when n passes through this critical value n_k , his measure of this energy when n is greater than n_k (accounting for about half the K absorption in addition to the L, M, N absorptions) implies an increase of corpuscular emission as n passes n_k , of the magnitude found in ionization experiments, and indicated by the plate experiments of Bragg and Porter.

BARKLA & SHEARER: The unsatisfactory nature of Sadler's results and the fragmentary nature of Bragg's (the whole argument being dependent on a single measurement) led Barkla and Shearer to examine the absorption of the K electrons. It was thought that when the frequency n of the exciting radiation was only slightly greater than n_k the critical absorption frequency in the element experimented upon, a decided loss of energy such as would

* Proc. Roy. Soc. 1911.

be expressed by the equation $\frac{1}{2}mv^2 = h(n - n_k)$ might be observed. In these experiments, however, the K electrons, *i.e.* those electrons associated with the emission of K characteristic radiation as distinct from other electrons, produced effects much smaller than had been expected from the results of Sadler, smaller even than the effect recorded by Bragg, and smaller than that shown by measurements of ionization. The *increase* in the energy of the corpuscular emission when the characteristic radiation was excited in the metal plate was only of the order of 100 per cent., *i.e.* the whole corpuscular emission was only about doubled. However, measurement showed that the difference between these additional K electrons as they emerged from the plate and the other electrons (L, M, N electrons) was in one case certainly very small, and in the other could not be detected at all.

The principal point which was regarded as established was that the K electrons which emerged from the metal plate were electrons whose maximum energy was given by hn approximately and not by $h(n - n_k)$. Also that the distribution of energy among the whole group was very similar to that among the other electrons.

These experiments thus showed that many of the K electrons had the whole energy of a quantum, or something very near to the full energy of a quantum, of primary radiation. But they did not indicate, as did the experiments above referred to, that the energy of these was approximately the whole energy of the corpuscular radiation. As far as these experiments went, there appeared the possibility of other more slowly moving electrons. These could not have been detected.

Energy Measurements.

The question as to whether the K electrons, many of which are evidently emitted with approximately, if not accurately, the energy hn of a full quantum of the primary radiation, constitute the whole of the K corpuscular radiation, was first investigated by Barkla * in a comparison of the ionization observed in C_2H_5Br when traversed by Ag K rays, with that calculated as produced by the swift electrons, the data for the latter being obtained from Sadler's experiments on corpuscular radiation from plates. The results showed that these corpuscles accounted for less than half of the total K ionization, indicating the possibility of other more

* Phil. Mag. August 1910.

slowly moving K electrons. If, however, we use Beatty's data obtained later for the corpuscular emission from selenium, it appears that approximately all the ionization is by such swiftly moving electrons.

Beatty shortly afterwards used data agreeing with Barkla's for the ionization, but values for the corpuscular emission about 2.4 times that observed by Sadler, and found that approximately all the ionization observed in SeH_2 was produced by the electrons such as were observed from a plate of selenium. Making a correction which we have previously pointed out, the observed and calculated values agree more closely than Beatty thought. Thus when Sr, Mo, Ag, Sn, and I radiations (K series) were used the rapidly moving corpuseles accounted for 120, 87, 84, 86, and 103 per cent. respectively of the ionization actually observed in SeH_2 , though this was almost entirely K ionization. There is here no room for an appreciable amount of corpuscular radiation of any other type.

It would perhaps be easy to attach too much importance to agreement of this kind, for the calculation depends too closely on so-called coefficients of absorption of corpuscular radiations in the material from which they are emitted. Such calculations as have been made, however, indicated that a large portion of the K corpuscular radiation consists of electrons of energy hn and not $h(n - n_k)$.

Thus Sadler, Bragg & Porter, and Beatty have all made measurements of the energy of corpuscular radiation emitted from metal plates. Unfortunately the results are very far from consistent, except in so far as they indicate the large effects produced by rapidly moving electrons even when n is only slightly greater than n_k . All three have expressed the energy (more precisely the total ionizing-power) of the electrons emerging from a plate exposed to a primary beam of X-rays, in terms of the energy of the electrons emitted by a layer of air 1 cm. in thickness when traversed by the same primary beam. Let this be R_1 when from the face of incidence, R_2 when from the face of emergence, and let $R = R_1 + R_2$.

We, however, wish to know the relative energies of the corpuscular radiations from layers of metal and air which produce the same absorption of the primary beam. In other words, we wish to know the fraction of the energy of the primary beam which is transformed into corpuscular radiation in the metal plate, as shown by what emerges from its surface. If the corpuscular radiation proceeded in a direction normal to the surface and were absorbed

exponentially with the distance as given by $I = I_0 e^{-\mu x}$, μ having the value μ_a' in air, μ_r' in the radiating plate, then it is quite easily seen that

$$R_{\mu_r'} = \frac{\text{energy corpuscular radiation from metal (thin sheet)}}{\text{energy corp. radiation from air of equal thickness}},$$

and

$$\begin{aligned} R_{\mu_a'} &= \frac{\text{energy corp. radiation emerging from thick metal plate}}{\text{energy corp. radiation emerging from a thick air plate}} \\ &= \frac{\text{energy of corp. radiation emitted by metal}}{\text{energy of corp. radiation from equal mass of air}} \end{aligned}$$

if the absorption of corpuscular radiation is proportional to the density of the absorbing substance.

Dividing the above by the ratio of the mass absorption coefficients of the primary X-radiation in metal and in air, we get the fraction

$$\frac{\text{energy corpuscular radiation from metal}}{\text{energy corpuscular radiation from air}}$$

for equal absorptions of primary beam. But the corpuscular radiation from air is a measure of the energy of the X-radiation absorbed in it*.

Now

$$\frac{\mu_r}{\rho_r} = \text{mass absorption coefficient of primary X-radiation in the metal};$$

also

$$\frac{\mu_a - \sigma_a}{\rho_a} = \text{mass absorption coefficient of primary X-radiation in air, after subtraction of the scattering coefficient } \frac{\sigma_a}{\rho_a}.$$

Thus

$$\begin{aligned} R_{\mu_a'} \div \frac{\mu_r / \rho_r}{\mu_a - \sigma_a} &= \text{fraction of energy of primary radiation transformed into energy of corpuscular radiation in the metal,} \\ &= \frac{k_r'}{\mu_r} \text{ say,} \end{aligned}$$

where k' is the coefficient of transformation of the primary X-radiation into corpuscular radiation in the metal.

We can thus determine the fraction of the energy of a primary beam appearing as corpuscular radiation, assuming that what emerges from the surface of the metal is a fair sample of the whole corpuscular radiation. Most of the

* n being much greater than n_k for air.

measurements were made on the radiation from one face alone, Sadler's and Bragg & Porter's from the face of incidence, Beatty's from the face of emergence; we have therefore as an approximation taken R as $2R_1$ or $2R_2$ as the case may be.

Regarding the assumptions, though the corpuscular radiation as measured (*i. e.* that emerging) consisted of rays covering the whole range of velocities from the maximum downwards, and these moved in all directions, the diminution of ionizing power was found by experiments (Sadler) to be connected with the thickness of the absorbing sheet approximately by an exponential law; also the proportionality of absorption with density of the absorbing substance seems to hold at least approximately, in such cases as those to which we wish to apply it. Table IV. gives the determinations on these assumptions from the results of Sadler, Bragg & Porter in curved brackets, Beatty in square brackets.

Beatty's results (for Ag and Se) are the most regular and definite. They indicate at once that when n is less than n_k , practically the whole of the absorption was accounted for by the corpuscular radiation as measured from the Ag plate; but when n was greater than n_k , the corpuscular radiation possessed a fraction increasing from about $1/2$ to the full energy of the absorbed primary radiation. These results agree almost perfectly with the conclusions from the ionization experiments, and find further support from the measurements of the energy of the characteristic radiation. These results seem to justify the calculation based on the plate experiments. They indicate that the corpuscular radiation such as emerges from the surface of a plate gives us a measure of the whole corpuscular radiation as detected in a gas.

There is no indication of the *large* diminution in the value k' which would have occurred when n slightly exceeds n_k if the K electrons had been ejected with energy much less than hn .

The results of Bragg & Porter (curved brackets), though not so regular, indicate the same thing. The values approximate to unity when n is less than or much greater than n_k , but when n is slightly greater than n_k (see columns for Fe, Ni, Cu, and Zn) somewhat smaller values are recorded. Yet the K absorption in these cases is

* Using Sadler's values of the absorption coefficients for corpuscular radiations.

TABLE IV.

Showing approximate fractions $\left(\frac{k'}{\mu}\right)$ of X-ray energy transformed into corpuscular radiation—as measured from metal plates. From Sadler, Bragg & Porter (curved brackets), Beatty [square brackets].

Radiation.	Al.	Fe.	Ni.	Cu.	Zn.	Se.	Ag.	Sn.
Fe	.106	very small.		very small.			.276 [1.06]	
Co	.128	"		"			.32	
Ni		.66		"			.364	
Cu		.6		.2			.42 [.96]	
Zn	.22 (.74)	.58 (.72)	(.72)	.52 (1.84)	(1.06)		.50 [1.0]	(.82)
As	.366 (1.16)	.50 (.74)	(.70)	.66 (.84)	(.78)		.74 [1.06]	(1.02)
Se	.430	.44		.450			.8	
Sr	.794	.36		.36		[.64]	.98	
Mo	1.2	.26		.22		[.69]	.84	
Rh	1.38						.72	
Ag	1.42	.24		.24		[.76]	.62	
Sn	1.62 (1.10)	.22 (1.10)	(.98)	.18 (.96)	(.94)	[.80]	.50 [.44]	(1.96)
I						[.98]		

almost the total absorption, which indicates that the K absorption is attended by an intense K emission from the plates. The energy of the fluorescent characteristic radiation would approximately account for the deficiency. Two values for Zn radiation on Cu and Sn radiation on Sn are evidently very high.

Sadler's results show remarkable variation from Beatty's and Bragg & Porter's. With increasing frequency of primary radiation, the value of $\frac{k'}{\mu}$ in Al rises steadily from a small value to too large a value; in Ag it rises and falls again; in Fe and Cu it commences with negligible values, suddenly and enormously rises, when n exceeds n_k , and subsequently falls away gradually with further increase of n . Though these results differ so markedly from Bragg's and from Beatty's, they indicate quite as pronouncedly that the result of the K absorption is the emission of an intense stream of electrons with energy approximately hn . Shearer's recent experiments, on the other hand, indicate little if any connexion between the electronic emission and characteristic radiations.

More recently, M. de Broglie (and Whiddington) have shown that groups of electrons ejected have energy given by $\frac{1}{2}mv^2 = hn - hn_k$. Unfortunately we do not yet know what fraction these are of the whole number of electrons ejected, or of the number of "K" electrons. In fact the method employed does not distinguish between the various groups of electrons except by their velocity.

Tentatively one of us suggested* that the electrons with energy $hn - hn_k$ were those ejected from the atom with energy hn which subsequently lost energy hn_k in passing through another atom, exciting in it the characteristic radiation of frequency n_k †. Such electrons would probably only form a small fraction of the whole number, and it seems very questionable whether they could produce such well-marked lines as those shown in the beautiful photographs obtained by M. de Broglie.

Our Plate Experiments.

The matter is of such importance theoretically, and the few results obtained by other experimenters on metal plates have been so remarkably inconsistent, that we determined to

* Solvay Conference, Brussels 1921.

† Or it might be ejected with energy hn from a certain system within the atom subsequently losing hn_k in another part of the same atom.

examine the emission of electrons from plates exposed to characteristic radiations of various frequencies including that of the characteristic radiations excited in the substance experimented upon, studying especially *the change* in the emergent corpuscular radiation as the frequency of the primary beam is increased from a value less to one greater than the critical absorption frequency for the plate. For when n is only slightly greater than n_k , the value of $h(n - n_k)$ is very small, so that the energy of ejection from the atom is presumably small. The effect of this is that very few such electrons can possibly emerge from the plate experimented upon. Thus, supposing n to be slightly greater than n_k , if the energy of emission of K electrons is given by $h(n - n_k)$

each K electron has only the fraction $\frac{n - n_k}{n - n_l, n_m, \text{ or } n_n}$
 $= \frac{n - n_k}{n}$ approximately of the energy of the other L, M, N electrons. But more than that, these K electrons can only emerge from a very thin layer of the order $\left(\frac{n - n_k}{n}\right)^2$ of the thickness of that from which the L, M electrons emerge. Thus the K electrons can only produce outside the plate an effect $\left(\frac{n - n_k}{n}\right)^3$ of that of an equal number of the other L, M, N electrons.

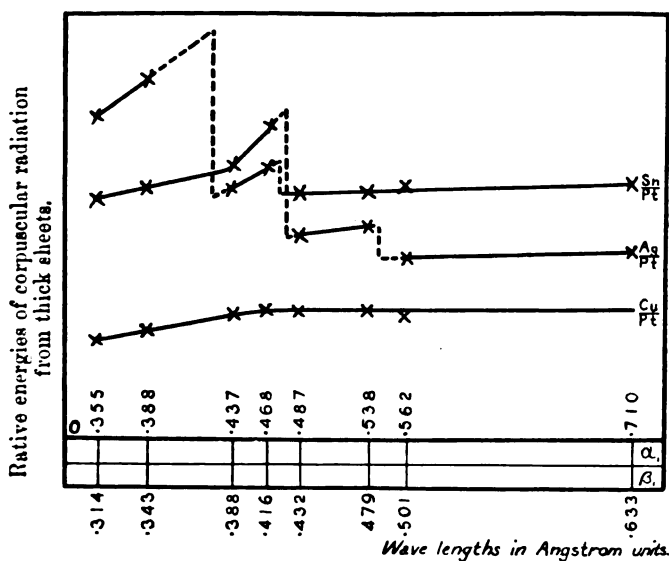
The effect of the K electrons would thus be inappreciable outside the plate when n exceeds n_k slightly. It would appear only very gradually as n increased, no increase being appreciable until n exceeded n_k by something of the order of 30 per cent. or 40 per cent. On the other hand, if the energy of the K electrons from the plate is given by hn , then when n passes n_k there is a sudden increase in the corpuscular radiation emerging from the surface, the K electrons producing ionization proportional to their number.

This experiment was performed using characteristic radiations of series K as exciting radiations. The metal plate experimented upon was placed at the end of an ionization chamber 10 cm. in length containing hydrogen. The front window was of aluminium faced internally with filter-paper. Thus the radiation passed through filter-paper, through the hydrogen, and on to the back plate. The direct ionization of hydrogen by X-rays was negligible, so that the whole ionization observed was that due to electrons from the two faces by which the beam entered and left the

chamber. The emission from the front face when this was of paper was also small, as was seen by performing the experiment with paper faces both front and back. Thus the ionization observed was that produced by electrons from the metal surface at the end of the ionization chamber. A standard for comparison had of course to be employed: this was obtained by using a metal, usually platinum, which has no characteristic radiation within the range of frequencies covered by primary radiations.

The results typical of those obtained from a large number of experiments of this kind are shown in fig. 1, in which the

Fig. 1.



energy of the emergent corpuscular radiation compared with that obtained under similar conditions from platinum is plotted against wave-length of the exciting radiation. It should be remembered that each radiation used in these experiments was a complex radiation, but may be regarded as consisting of only two distinct components, known as the K_α and K_β radiations— K_β the radiation of higher frequency having an intensity about one-fourth that of the K_α radiation. In the figure, the wave-lengths of both the α and β constituents are shown along the horizontal axis, the α constituent being exactly to scale, the β only approximately so, as there is a slight deviation from proportionality of the two. In proceeding from longer to

shorter wave-lengths, the K_β radiation is the first to pass the critical absorption wave-length in the substance experimented upon.

The principal features of interest in the curves are the following :—

Copper.—The corpuscular emission from copper varies little from proportionality with that from platinum. This is as it should be, as there is no spectral line of either within the range covered by these experiments. Even the small gradual diminution of the ratio with increasing frequency at the higher frequency end, would need confirmation. More direct experiments did not show such a variation : we shall return to this again.

Silver.—In the curve for silver, passing from longer to shorter waves two distinct rises occur due to the effects of the two components of the K radiation, in each case when the effective component passes through the critical absorption wave-length, which is somewhat shorter than that of the K_β line for silver.

The relative magnitudes of these increases are, as nearly as can be observed, in the same ratio as the relative intensities of the two constituents themselves.

The total increase in the energy of corpuscular radiation when both constituents pass the critical frequency is about 100 per cent., the rise actually observed with Sb radiation being about 85 per cent. In the case considered, if the energy of the K electrons were given by the relation $\frac{1}{2}mv^2 = h(\nu - \nu_k)$ and if all the additional energy absorbed—the K absorption—were transformed into this radiation, the increase observed would be only of the order of 3 per cent.

It must be remembered, however, that the characteristic radiation excited in the plate must itself give rise to a corpuscular radiation when absorbed in its own substance. Thus for instance, when Sb radiation falls on Ag and causes it to emit Ag X-rays (of series K), these Ag X-rays themselves produce an emission of electrons which on either theory possess energy differing little from $h\nu$. Calculation (see below *) shows that this would account for a rise of

* Thus the intensity of the exciting primary beam at a depth x is given by $I = I_0 e^{-\mu_1 x}$. This excites characteristic X-radiation, the rate of emission of energy from a thin slab of unit area and thickness δx being $k I_0 e^{-\mu_1 x} \delta x$, where k is the transformation coefficient.

The energy of the characteristic radiation passing out through the surface in a direction between the angles θ and $\theta + \delta\theta$

$$= \frac{2\pi \sin \theta \cdot \delta\theta}{4\pi} k I_0 e^{-\mu_1 x} \delta x (e^{-\mu_2 x \sec \theta}) \times k_2' t_2 \sec \theta,$$

where k_2' is the coefficient of transformation of characteristic X-radiation

something like 35 per cent. in the corpuscular emission from the silver plate, leaving say a 50 per cent. rise due to the more direct action of the primary X-rays. The order of magnitude of this secondary effect is, however, too close to that measured to enable us to arrive at confident conclusions without further evidence. In order more directly to test this point, we made experiments on very thin sheets (thickness .0003 cm.) from which the secondary effect of the fluorescent radiation was only about $\frac{1}{3}$ of that from the thick sheet; consequently the corpuscular emission due to this was reduced by $\frac{2}{3}$. The difference between the effects from thick and thin sheets was experimentally found to be quite appreciable (see fig. 2), the increase for the thin sheet being diminished to about 60 per cent. From these results again it might be concluded that the effect produced by the more direct action of the primary rays—that is, the sudden increase occurring in the ionization produced outside the silver plate, caused by electrons ejected under the direct influence of the primary radiation when

into corpuscular radiation, and t_2 is the effective thickness of the surface layer contributing to the corpuscular radiation emerging.

The energy of corpuscular radiation emitted per sec. from the surface and due to the secondary characteristic radiation proceeding in direction between θ and $(\theta + \delta\theta)$

$$= \frac{1}{2} k k_2' t_2 I_0 \tan \theta \delta\theta \int_0^d e^{-(\mu_1 + \mu_2 \sec \theta)x} dx,$$

where d is the thickness of the plate,

$$= \frac{1}{2} \frac{k k_2' t_2 \tan \theta}{\mu_1 + \mu_2 \sec \theta} I_0 \{1 - e^{-(\mu_1 + \mu_2 \sec \theta)d}\} \delta\theta.$$

$\therefore$ Total energy emission per sec. in corpuscular radiation due to the secondary characteristic X-radiation

$$= \frac{1}{2} k k_2' t_2 I_0 \int_0^{\pi/2} \frac{\sin \theta}{\mu_1 \cos \theta + \mu_2} \{1 - e^{-(\mu_1 + \mu_2 \sec \theta)d}\} d\theta.$$

The corpuscular emission due to the direct action of the primary X-radiation is $k_1' t_1 I_0$, where k_1' is the coefficient of transformation of the primary into corpuscular radiation, and t_1 is the effective thickness of the layer contributing to the surface emission.

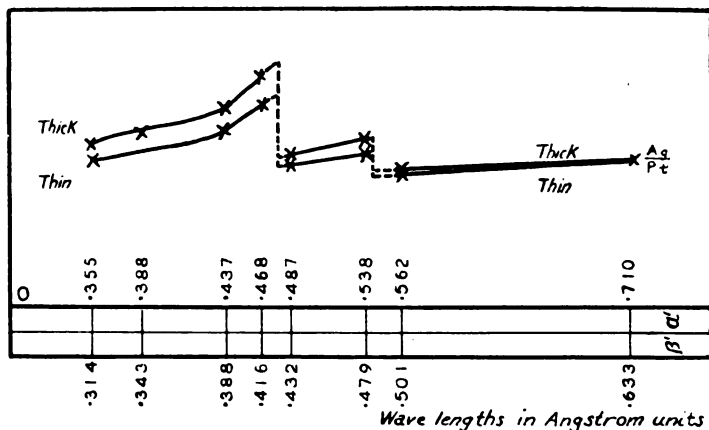
Now the only assumption we need make in order to obtain a fairly accurate measure of the effect of the corpuscular radiation excited by the secondary characteristic X-radiation, is that the fraction of the energy of corpuscular radiation emerging through the surface from the very thin effective layer is the same when the exciting X-radiation spreads in all directions as when it passes through the thin sheet normal to the surface,—that is, of course, for equal absorptions of energy in the thin sheet.

All the evidence points to the conclusion that for a given absorption of energy of a definite X-radiation in the surface layer, the difference between the two would be small.

Assuming exact equality, then, if there were no true K corpuscular

its frequency slightly exceeded its critical value—was not more than about 50 per cent. Ionization-pressure curves were obtained to test if the increase were due to swiftly-

Fig. 2.



moving electrons. These left no doubt that the additional ionization was due neither to a soft X-radiation nor to a corpuscular radiation of slowly-moving electrons. Energy considerations alone show the latter to be impossible except by a release of atomic energy, as the intensity would need to be enormous to produce the observed effects from the

emission, that is, if all the observed rise were due to the secondary characteristic radiation,

$$\frac{k_2'}{k_1'} \text{ would } = \frac{\mu_2}{\mu_1} = \frac{\lambda_2^3}{\lambda_1^3} \text{ fairly accurately,}$$

and

$$\frac{t_2}{t_1} = \frac{\lambda_1^2}{\lambda_2^2},$$

from Whiddington's Absorption Law for rapidly moving electrons and the Planck-Einstein relation $\frac{1}{2}mv^2 = h\nu$.

Thus the ratio $\frac{\text{secondary characteristic radiation effect}}{\text{primary radiation effect}}$ would be

$$\frac{1}{2}k \frac{\lambda_2}{\lambda_1} \int_0^{\pi/2} \frac{\sin \theta}{\mu_1 \cos \theta + \mu_2} \{1 - e^{-(\mu_1 + \mu_2 \sec \theta) d}\} d\theta.$$

The coefficients of absorption μ_1 and μ_2 of the primary and secondary radiations in silver are known accurately; the wave-lengths of these K radiations are also known; k is known for the transformation of radiations into characteristic radiations in various metals, and in the case of Sb radiation of K series in Ag is about .4. Hence the above fraction may be calculated.

exceedingly thin layer of metal which would be effective. The same argument would apply to very soft characteristic radiations such as would be completely absorbed in 10 cm. of hydrogen.

Thus the sudden rise in the corpuscular radiation from silver when the exciting radiation is of slightly higher frequency than the K_β radiation of silver, is very much smaller than might have been expected from the results obtained from previous experiments, but again such effect as there is cannot be explained by the emission of electrons with energy $h(n-n_k)$.

Tin.—The curve showing the corpuscular emission from Sn relative to that from Pt is similar to that from Ag, the discontinuities occurring at a higher frequency corresponding to the higher critical absorption frequency.

These results, then, only partially support our previous conclusion drawn from the results published by other observers. They indicate that some electrons emitted in association with the K fluorescent radiation possess the full energy hn , or at any rate a value very near to this. But it appears from these experiments that this radiation does not account for anything like the whole of the additional energy absorbed, for the increase in absorption is something of the order 700 per cent. Thus the fraction of this energy absorbed—the K absorption—appearing in the rapidly moving corpuscles when n is slightly greater than n_k is only of the order of 7 per cent. instead of a possible 50 to 60 per cent. (The energy of the characteristic X-radiation emitted appears by extrapolation from Sadler's results to be of the order of 40 per cent. of the K absorption.)

The difference between 7 per cent. and a possible 60 per cent. for the corpuscular radiation (or nearly 50 per cent. actually observed by the ionization method in C_2H_5Br) suggests the possibility of an emission of other electrons with energy considerably less than hn , as those observed by de Broglie. These would not escape from plates in sufficient number to produce an appreciable ionization outside, but in gases they would produce an ionization proportional to their energy.

It is difficult to reconcile our results with the results of measurements of Sadler, of W. H. Bragg, and of Beatty, which all led to the conclusion that approximately all the electronic emission was in the form of electrons with energy hn . These experiments have, however, been made

upon other elements. The investigations are being continued, but the discrepancies suggest the influence of factors not hitherto taken into consideration.

Again, the corpuscular emission as observed from Ag and Sn plates (compared with the standard Pt) appears to fall off again to a certain extent as n increases beyond the critical value n_k , and when n is considerably greater than n_k the corpuscular emission becomes very small. This is not what we expected, for it accentuates the discrepancy between energy absorbed and that re-emitted in the form of the rapidly moving electrons. There is, however, agreement in this respect with the results obtained by Sadler for Fe and Cu. It might of course be accounted for by a possible selective absorption of electrons moving with energy greater than hn_k in an element with characteristic frequency n_k , but this effect is probably very small.

It appears, therefore, that the electronic emission which we have been studying is most intense when the frequency of the primary X-radiation is very near to the critical absorption frequency.

SUMMARY.

The energy of the corpuscular radiation emitted by metal plates when exposed to X-radiation of varying frequency has been investigated by a simple method (previously used by one of the authors in a few isolated cases). The results differ substantially from those obtained by other investigators by different methods.

They show two independent discontinuities in corpuscular emission due to α and β constituents of the K radiation when this was used to excite corpuscular emission.

They show that few K electrons, *i. e.* those electrons emitted in exclusive association with the K characteristic radiation whatever their origin, have energy of the order hn , where n is the frequency of the exciting radiation.

From silver and tin, these electrons (unless their full energy is concealed by a selective absorption of improbable magnitude in the substance emitting them) are altogether insufficient in number to account either for the observed increase in ionization, *i. e.* for the whole K ionization when the substance is in the gaseous form, or for the full energy of characteristic radiation on the basis of one quantum of characteristic radiation for one high-speed electron.

In this respect these results differ most markedly from

those obtained by previous experimenters on the emission from metal plates.

The inadequacy of these electrons thus points to the importance of the part being played by other electrons with energy $h(n-n_k)$, such as found by de Broglie; these would not be detected by the plate experiments.

On the other hand, the ionization experiments of Barkla and the results of experiments by Sadler, by Beatty, and Bragg, on the emission of electrons from metal plates, all indicate that the bulk of the energy in the corpuscular radiation—the K corpuscular radiation—is in electrons of energy approximately hn . Such experiments have been made, however, in substances of lower atomic weights. These substances are now being studied by more exact methods.

II. *An Experimental Determination of the Rate of Decay of the Short-Life Product Radium C'.* By J. O. JACOBSEN, *Physicist at the Medical Radium Institute, Copenhagen* *.

IN 1911 Geiger and Nuttall† found a simple relation between the transformation constant λ for radioactive substances emitting α -rays and the range R of the α -rays, namely, that the points obtained by plotting $\log \lambda$ against $\log R$ are situated nearly on a straight line, or

$$\log \lambda = a + b \log R,$$

where the constant a has somewhat different values for the three radioactive families. More accurate measurements carried out later by Geiger‡ show that the formula is not exact, as within each of the radioactive families deviations are found which can hardly be explained by errors of measurement. The agreement between the formula and the measurement is best for the Uranium-Radium family, where, among the substances for which both λ and R are known with some accuracy, only the emanation with certainty falls outside the curve.

The best agreement with the experiments is obtained with the following values of the constants :

$$a = -41.0, \quad b = 59.3.$$

* Communicated by Prof. Sir E. Rutherford, F.R.S.

† Phil. Mag. xxii. p. 613 (1911).

‡ Zs. für. Phys. viii. p. 45 (1921-22).

The range of the α -rays from RaC' is 6.608 cm. ; with the above values of a and b this gives for the transformation constant

$$\log \lambda = 7.7, \quad \lambda = 5 \cdot 10^7 \text{ sec.}^{-1},$$

or the half-period value $T = 0.35 \cdot 10^{-7}$ sec. The decay of a substance like this cannot of course be examined by ordinary experimental means; in fact, if one could prepare pure RaC', the substance would practically have disappeared 10^{-6} sec. after the preparation. On the other hand, the peculiar character of the formula and the fact that no successful theoretical explanation has hitherto been given, invite further experimental investigation. If a direct measurement of the transformation constant λ for RaC' could be carried out, the values of λ for which the validity of the formula could be tested would be extended from 10^{-18} to 10^7 , the value of λ deduced from the formula supposed to be correct.

Experimental Method.

The value of λ is (supposedly) of the order of magnitude 10^7 sec.^{-1} . In seeking for a suitable method to measure λ the problem is to find a known quantity of the same order of magnitude, with which λ can be compared. The most suitable quantity for this purpose seems to be the velocity of the recoil atoms from RaC. If M and V denote mass and velocity of the recoil atom, V is calculated from

$$\frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \cdot v = M \cdot V,$$

where m_0 is the mass and v the velocity of the β -particle. In the calculation of V the difficulty at once appears that the β -rays from RaC are complex, so that the value of v to be introduced cannot be fixed. Without entering into a detailed discussion of the origin of the β -rays, we may suppose that the primary β -rays from a definite radioactive substance all have the same velocity, so that at least part of the β -rays from RaC are secondary. Further, we may suppose that the primary β -rays have a higher velocity than the secondary ones, so that the value of v to be introduced into the formula is to be chosen from among the highest values found for the velocities of the β -rays. The highest

value which has been measured seems to be $v=0.996.c.*$. From this value we obtain

$$V=8.4 \cdot 10^5 \text{ cm./sec.}$$

Too much stress should not be laid on this special value for V , as it is chosen somewhat at random, but for the present it may be used to illustrate the experimental method.

Consider a plate covered with RaC . From the plate a stream of atoms of RaC' will be sent out moving with a velocity of $8.4 \cdot 10^5 \text{ cm./sec.}$ When such a recoil atom has moved a certain distance, it is transformed into an atom of RaD with the emission of an α -particle, which may be detected on a zinc-sulphide screen. By measuring the diminution of the number of RaC' atoms with increasing distance from the plate, the transformation constant λ of RaC' may be determined from the velocity V of the recoil atoms or *vice versa*.

For the decay of RaC' we have

$$n=n_0 \cdot e^{-\lambda t},$$

where λ from the Geiger-Nuttall formula is calculated to be $3.2 \cdot 10^7$. By introducing $t=\frac{\chi}{V}$, where χ is the distance from the active plate and V the velocity of the recoil atoms, we get

$$\log_e \left(\frac{n_0}{n} \right) = \frac{\lambda}{V} \cdot \chi.$$

As the number of α -particles emitted is proportional to the number of atoms present, n may denote the number of scintillations per minute on a suitably placed zinc-sulphide screen: thus, by plotting the logarithm of the number of scintillations against the distance from the active plate, the curve should be a straight line, whose slope determines $\frac{\lambda}{V}$.

The Experiments.

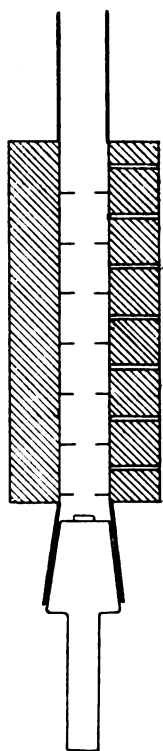
When carrying out the experiments screens must be placed in a suitable way, so as to obtain firstly an approximately parallel beam of recoil atoms, and secondly so that the α -particles observed are emitted in a direction perpendicular to that of the recoil atoms. After some trials to find

* Danysz, *Le Radium*, iii. p. 949 (1913); Rutherford, *Phil. Mag.* xvi. p. 717 (1913).

suitable dimensions of the apparatus, the following form was chosen:—

The apparatus consisted of a brass tube of square cross-section and 10 mm. internal diameter (fig. 1), the thickness of the walls being about 10 mm. In one side of the tube a number of slits 1 mm. in width were cut 6 mm. from one another. The extension of the slits perpendicular to the paper was 10 mm. The slits were closed by a mica leaf with 3.5 cm. air equivalent, fastened with sealing-wax on the outer side of the tube. Half way between the slits a number of screens with square openings 4×4 mm. were placed to prevent reflexion from the walls of α -particles coming from the active source. This was a nickel plate, which was placed in a cone in the lower end of the apparatus. The other end of the brass tube was connected to the pump, McLeod manometer, and an arrangement for letting in small quantities of air. Mercury vapours were kept away from the apparatus by a U-tube immersed in liquid air. The zinc-sulphide screen was attached to a microscope which could be moved in vertical direction.

Fig. 1.



As radioactive material it is necessary to use pure RaC (not active deposit). The active deposit on a metal plate is not situated solely on the surface, but, on account of the recoil from RaA, the RaB (and RaC) atoms are spread uniformly over a layer whose thickness is the range in the metal of the recoil atoms from RaA (of the order of magnitude 10^{-5} mm.). This is of no importance when working with α -rays, but in these experiments it is essential that the active material should be situated on the surface of the metal on account of the smallness of the energy of the β -rays; in fact, when using active deposit, the RaC' atoms would have all velocities from zero to a maximum value.

RaC was prepared in the following way:—About 100 millicuries of emanation were collected in a glass tube over mercury and left there for 3–4 hours. The emanation was then pumped off, and the active deposit dissolved in 1–2 c.c. of diluted hydrochloric acid. When placing a polished nickel disk in the hot solution for some minutes, RaC is obtained on the disk. To obtain pure RaC it is necessary to

wait until RaA has decayed. To avoid radioactive contamination the glass tube was heated with a Bunsen burner while the emanation was pumped off, and the nickel disk after activation was washed in distilled water and alcohol, and afterwards heated for a few minutes in a vacuum. The metal is attacked somewhat by the acid, though not much, and a polished plate as a rule keeps completely bright; only in a few cases was the plate slightly stained. In this way deposits with a γ -activity of about 5 mgrs. could be obtained. When the plate had been prepared, it was placed in the cone and the pump set in action. After 5 minutes pumping the pressure as a rule was lower than 0.0001 mm., and the measurements could be commenced. The microscope, with the zinc-sulphide screen, was placed in front of one of the slits, where the number of scintillations had a suitable value (as a rule No. 3 or 4 from below). The number of scintillations was counted, the time for each measurement being noted. When a suitable number of α -particles (100-400) had been counted, the microscope was moved downwards to the next slit, and the measurement repeated, etc.

The results now have to be corrected for the decay of the active source and for the fact that the solid angle, over which the beam of recoil atoms extends, changes when moving from one slit to another. As already mentioned, the screens all had the same aperture, 4×4 mm., so that the solid angle over which the beam of recoil atoms extends is inversely proportional to the square of the distance from the source to the corresponding screen. The following figures, which are taken from an actual experiment, may serve as an illustration :—

Slit No.	d_1 .	d_2 .	N_0 .	n .
4	25 mm.	21.8 mm.	13	6.2
3	19 "	15.8 "	...	...
2	13 "	9.8 "	195	18.7
1	7 "	3.8 "	1800	26.0

d_1 is the distance from the source to the slits, d_2 the distance from the source to the corresponding screens, N_0 is the number of scintillations in 100 seconds corrected for the decay of the source, under n is quoted $10^{-5} \cdot N_0 \cdot d_2^2$, n thus being proportional to the number of atoms transformed per unit time. If $\log_e n$ is plotted against d_1 , an approximately straight line is obtained, the slope of which is 0.81. The result of this experiment thus is $\frac{\lambda}{V} = 0.81$.

The question now arises whether the scintillations observed

are really due to α -particles being expelled from recoil atoms, and are not for instance due to α -particles coming from the active source and deflected by the walls and the edges of the screens. It is, however, very easy to make a control experiment on this point by letting a small quantity of air into the apparatus. On account of their small energy the recoil atoms will be stopped at a short distance from the source, at a pressure at which the α -particles will not suffer any sensible decrease of velocity. The number of α -particles counted usually was 10-60 per minute. By letting air into the apparatus to a pressure of about 1 mm. of mercury, the number of scintillations went down to 1-5 per minute, and when the air was pumped out, the number of scintillations went up to the former value.

The experiments hitherto performed have given values for $\frac{\lambda}{V}$ lying between 0.8 and 1.2 with a mean value of $\frac{\lambda}{V} = 1.0$.

On account of extraneous circumstances the experiments must be postponed for some time, the uncertainty of the result thus being rather great. As will appear from the sequel, this, however, is not essential for the discussion of the result.

If in $\frac{\lambda}{V} = 1.0$ we put $V = 8.4 \cdot 10^5$ (corresponding to a velocity of 0.996 of the β -rays), as result of the measurements is obtained

$$\lambda = 8.4 \cdot 10^5$$

or

$$\log_{10} \lambda = 5.9,$$

while the value predicted by the Geiger-Nuttall formula is

$$\log_{10} \lambda = 7.5.$$

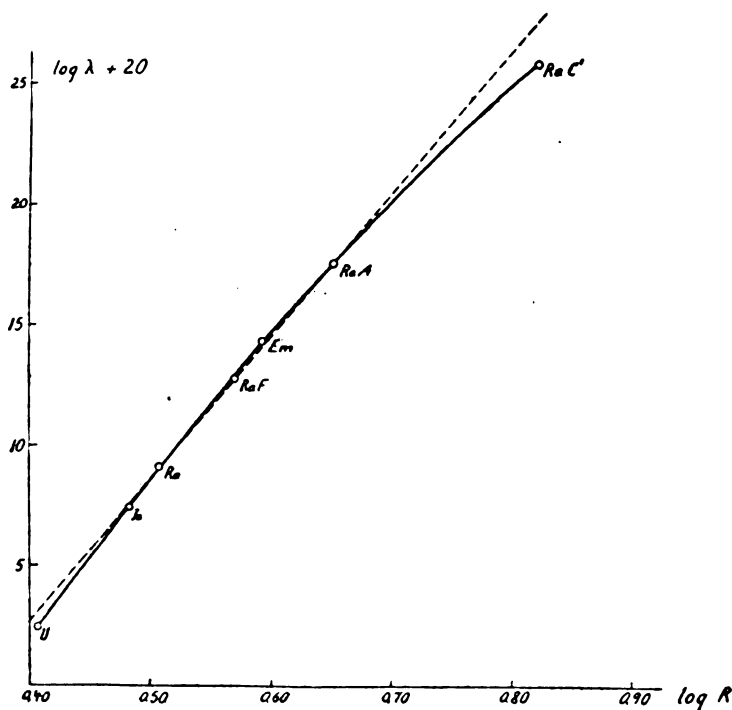
To see if the agreement between these values is satisfactory, consider a little more closely the quantities λ and V . A change in the experimental value for $\frac{\lambda}{V}$ of 100 per cent. would only give a change in $\log \lambda$ of about 6 per cent., thus being of no importance. If V is calculated from $\frac{\lambda}{V} = 1.0$ and $\log_{10} \lambda = 7.7$, we get

$$V = 5 \cdot 10^7,$$

a value which is 60 times greater than $V = 8.4 \cdot 10^5$, which has hitherto been used. Consequently, if the value of λ predicted by the Geiger-Nuttall formula is correct, the

momentum of the primary β -rays from RaC should be 60 times greater than corresponding to $v=0.996c$. Even if it may be considered as questionable whether by the experiments hitherto performed there has been any possibility for measuring so high velocities, because the deflexion of an electrified particle in a magnetic field is inversely proportional to the momentum of the particle, so that very strong magnetic fields would be required, it would certainly appear very improbable that such hard β -rays should be emitted from RaC. From these considerations it appears, therefore, that the value of λ predicted by the Geiger-Nuttall formula is definitely too high.

Fig. 2.



On the other hand, the value of λ calculated by the Geiger-Nuttall formula is not determined very exactly. The fact that the emanation definitely falls outside the curve indicates that the formula is only a first approximation, an assumption which is supported by a closer inspection of the figures. On fig. 2 the values of $\log \lambda$ given by Meyer

and v. Schweidler are plotted against $\log R$ taken from Geiger's paper *. The value of λ for RaC' is the one which is obtained by the present experiments, using $V = 8.4 \cdot 10^8$ for the velocity of the recoil atoms. The straight line (dotted) represents the Geiger-Nuttall formula. It is at once obvious that a slightly curved line gives a better agreement with the experimental values. By these considerations we are led to the assumption that the function $\lambda = f(R)$ in reality is represented by some slightly curved line, although the experiments yet are not sufficiently exact to settle this point definitely.

For the corresponding product of the Thorium sequence ThC', the value of λ predicted by the Geiger-Nuttall formula is about $10^{-11} \text{ sec}^{-1}$. If this value is of the right order of magnitude, it seems impossible to obtain a comparison with the velocity of the recoil atoms from ThC, because the proportion $\frac{\lambda}{V}$ will differ widely from unity, since V certainly cannot be much more than 10^8 . However, the experiment ought to be performed, but at present sufficiently strong Mesothorium preparations are not at the author's disposal.

Control Experiments.

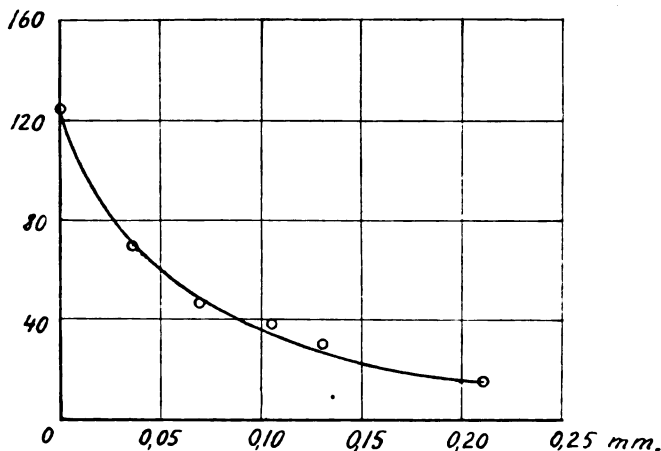
The reliability of the results would be increased if the velocity of the recoil atoms could be determined without knowing the velocity of the β -rays. This may be done either by determining the deflexion of the recoil atoms in a magnetic field or by measuring the range in air. The first possibility involves the difficulty that it is unknown whether the recoil atoms from RaC in a vacuum possess an electric charge, and, in addition, very strong magnetic fields would be required. If the recoil atoms have a single electric charge, they will suffer the same deflexion as the corresponding β -rays, but owing to the rapid diminution of the number of recoil atoms with increasing distance from the source, it is necessary to use circles with a small radius. A determination of the range is more easily carried out, but requires a calculation of the connexion between range and velocity. [Experiments to determine the range in air are in progress.]

Although the experiments at this point are rather

* Geiger, *l. c.*

incomplete, a preliminary result may be given here (fig. 3). The microscope was set at a fixed distance (12.7 mm.) from the source, and the scintillations counted with air at different pressures in the apparatus; intermediate countings in vacuum were taken for control, showing that the decay of the source took place according to a half-value period of 19.5 minutes.

Fig. 3.



In fig. 3 the number of scintillations in 100 seconds, corrected for the decay of the source, are plotted against the pressure (in mm. Hg) in the apparatus. The number of scintillations falls off approximately exponentially with increasing pressure.

Summary.

1. RaC' has been observed in an isolated state, the emission of α -particles having been observed under such circumstances that the α -particles cannot be due to any other substance.

2. For the transformation constant λ of RaC' is found

$$\log_{10} \lambda = 5.9,$$

a value which, by a comparison with the other products of the Uranium-Radium sequence, suggests a modification of the Geiger-Nuttall formula.

The experiments were carried out at the Institute of Theoretical Physics with material from the Medical Radium Institute. The author wishes to express his thanks to the Managing Board and to Professor Bohr for the facilities afforded.

III. *A Determination of the Vapour Pressures of Cæsium and Rubidium, and a Calculation of their Chemical Constants.* By D. H. SCOTT, D.Phil.*

THIS paper describes the determination of the vapour pressures of Cæsium and Rubidium between 50° C. and 130° C. with the aid of a vibrating quartz fibre manometer. From the figures obtained the chemical constants of the two metals were calculated and found to be in agreement within the experimental error with the formula

$$C = 1.5 \log M + C_0$$

(where C is the chemical constant, M the molecular weight, and C_0 the "absolute chemical constant"). The work was undertaken not so much with the object of verifying this formula—which may fairly be regarded as established—as in the hope of supplying further information about the vapour pressures of monovalent elements, which may be of value in future work on the nature of the inter-atomic forces.

The original quartz fibre manometer described by Haber (*Zeitschrift für Elektrochemie*, xx. p. 296 (1914)) consists essentially of a quartz fibre about 4 mm. thick and 9 cm. long, supported inside a wide glass tube. The fibre is observed through a microscope and illuminated from the side. When the fibre is at rest a sharp line of light is seen in the field of view, and if the fibre is set in vibration this line broadens out into a band whose width can be measured on a scale in the eyepiece of the microscope. The method of using the instrument consists in observing the time taken for the amplitude of vibration to diminish to a definite fraction of its original value. This time T is connected with the pressure by the relation

$$b = T(\Sigma p M^{1/2} + a), \quad \dots \dots (1)$$

where a and b are constants determined by calibration against a McLeod gauge. The term $\Sigma p M^{1/2}$ is formed by adding together the products of the partial pressures of the various gases present and the square roots of their respective molecular weights. In Haber's original gauge the fibre was set vibrating by tapping the instrument with the finger. This method did not prove at all satisfactory, as it was found extremely difficult to produce vibrations in a plane. As a rule a compound vibration was set up which made the edges

* Communicated by Prof. F. A. Lindemann, F.R.S.

of the observed band of light oscillate to and fro in such a way that accurate reading was impossible. The problem was finally solved by fusing about three turns of very fine iron wire on to the tip of the quartz fibre so that the vibration could be controlled with an electromagnet operated by a tapping key. By this means it was possible to produce vibrations regularly in a plane, so that the edges of the observed band of light were quite sharp and its width could be accurately measured. The extra weight of the iron tip increased considerably the time required for the amplitude to diminish by its definite amount, and in consequence a somewhat thicker quartz fibre was used ($7\text{ mm.} \times 8.3\text{ cm.}$ for the manometer used for the measurements on mercury; $8\text{ mm.} \times 8.9\text{ cm.}$ for that used for the cesium and rubidium).

The fibre was fused directly on to a quartz rod about 6 mm. thick and 6 cm. long. The method of fixing this quartz rod into the outer glass-work will be seen clearly in fig. 1. AB is a glass tube which fits the quartz as closely as possible. It is constricted very slightly at B. The quartz with the fibre attached is introduced from the top and tapped well down. The glass tube is then sealed off at A. This has been found to make a sound mounting and has proved quite satisfactory. The quartz rod was ground flat on two sides so that any gas in the tube above could pass out freely when the apparatus was being exhausted.

Experience has shown that one precaution is necessary with this mounting. Whenever the apparatus is heated to get gas out of the glass the gauge must be turned into a horizontal position. If this is not done, the quartz rod sinks down when the apparatus is hot and cracks the glass near the constriction on cooling.

In practice the time observed was that required for the band of light to diminish in width from 50 scale-divisions (about 0.63 mm.) to 40 scale-divisions, *i. e.* the time required for the amplitude to diminish to $\frac{4}{5}$ of its original value. Three readings at each pressure were taken, and as a rule the difference of the extreme readings was not more than 1.5 per cent.

The manometer was calibrated against a McLeod gauge of the usual pattern, with a multiplication factor of $6.64 \cdot 10^{-5}$. A trap immersed in liquid air prevented any mercury vapour from getting from the McLeod gauge into the manometer, and the total pressure in it was then that given by the McLeod gauge. Readings of the two gauges were taken at various pressures, and from these the constants

a and b in the equation $b = T(\Sigma p M^{1.2} + a)$ were determined. For air $\Sigma p M^{1.2} = 5.38p$, so that the calibration equation is therefore

$$b = T(5.38p + a). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We can calculate the most probable values of a and b in the usual way by solving the normal equations

$$nb = 5.38 \Sigma p_1 T_1 + a \Sigma T_1,$$

$$b \Sigma T_1 = 5.38 \Sigma p_1 T_1^2 + a \Sigma T_1^2,$$

where n is the number of readings.

Table I. shows the calibration readings for the gauge which was actually used in the determination of the vapour pres-

TABLE I.
Calibration Readings.

	T (seconds).	p (mm. of Hg).	$\theta_{\text{Abs.}}$	$\theta'_{\text{Abs.}}$	$p' (= p \sqrt{\frac{\theta'}{\theta}})$	$p'_{\text{Calc.}}$
1	507	$< 10^{-3}$	288.6	423.0	$< 10^{-3}$	$5.1 \cdot 10^{-6}$
2	370	$2.48 \cdot 10^{-4}$	288.0	421.3	$3.00 \cdot 10^{-4}$	$3.10 \cdot 10^{-4}$
3	274	5.12	288.0	426.8	6.24	6.38
4	208	8.76	287.8	421.5	$1.06 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$
5	188	$1.01 \cdot 10^{-3}$	288.0	423.6	$1.22 \cdot 10^{-3}$	1.22
6	150	1.39	288.1	425.7	1.69	1.68
7	141	1.52	287.5	424.3	1.84	1.83
8	125	1.77	287.5	423.5	2.15	2.18
9	113	1.71	287.4	422.3	2.08	2.44
10	86	2.81	287.7	421.0	3.40	3.40
11	68.2	3.68	288.0	426.1	4.48	4.41

Readings 1 and 9 not used in the determination of most probable values of a and b .

$$\begin{aligned} b &= T(5.38p' + a), \\ \text{whence } b &= 1.863, \\ a &= 3.361 \cdot 10^{-3}. \end{aligned}$$

tures of caesium and rubidium. While taking the measurements on caesium and rubidium the fibre manometer had to be kept at a temperature of about 150°C. to prevent any of the metal condensing in it. In order to eliminate any error that might be caused by change of the constants a and b with temperature the gauge was calibrated at 150°C. The air pressure in the gauge was in consequence higher than

that shown by the McLeod. The values given by the McLeod were therefore multiplied by $\sqrt{\frac{\theta'}{\theta}}$ (θ' =temp. of fibre manometer, θ =temp. of rest of apparatus) to give the true pressure inside the fibre manometer.

The last column in Table I. gives the results of re-calculating by equation (2) the pressures corresponding to the values of T given in the first column.

Before proceeding to the measurement of the vapour pressures of cæsium and rubidium it was decided to carry out a check determination of the vapour pressure of mercury. If readings of both the gauges are taken when the trap is not in liquid air, the vapour pressure of mercury at room temperature can at once be determined. For the only gases in the apparatus are air and mercury vapour; the fibre manometer gives the total pressure, and the air pressure is given by the McLeod gauge. The fibre manometer actually used in this determination unfortunately cracked during heating preparatory to being used for cæsium and rubidium—and it has not been thought worth while to give the calibration readings in full. The values of the constants in equation (1) were $a=2.67(4).10^{-3}$ and $b=1.97(0)$. The results obtained are shown in Table II. T is the time in seconds required for the amplitude of vibration of the fibre to diminish from 50 to 40 scale-divisions. p is the air pressure as shown by the McLeod gauge, θ the temperature of the apparatus, and π_{θ} the vapour pressure of mercury at $\theta^{\circ}\text{C}$. The last column gives the value of π corrected to 20°C .

The consistency of these results compares favourably with those obtained by Haber (*Zeitschrift für Elektrochemie*, xx. p. 301 (1914)). He gives the value for π_{20} as $1.26.10^{-3}$. This is the result of a weighted mean of two series of observations. The first series consists of seven readings giving results varying between .00112 and .00152, the second of four readings giving results between .00103 and .00140.

At the same time the mean value .00130 is rather higher than both Haber's (.00126) and Knudsen's (.00119). Egerton (*Phil. Mag.* xxxix. Jan. 1920), after a careful examination of the experimental evidence, concludes that the true value lies between .00119 and .00126—probably nearer Knudsen's value than Haber's. But it is interesting to note that the most recently published accurate determination of the vapour pressure (Hill, 'Physical Review,' vol. xx. p. 266 (1922)) gives the value of π_{20} as .00182.

TABLE II.
Vapour Pressure of Mercury.

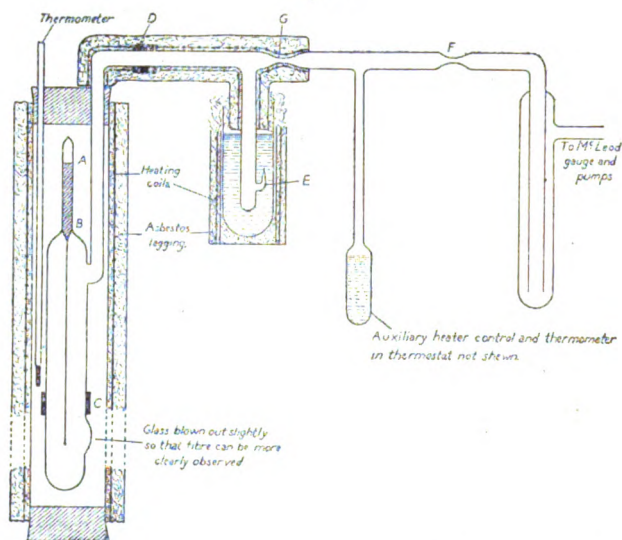
T.	p .	6° C.	π_{θ} .	$\pi_{20^{\circ}}$.
139	$2.66 \cdot 10^{-3}$	15.0	$8.02 \cdot 10^{-4}$	$1.25 \cdot 10^{-3}$
125	7.30	15.3	8.96	1.36
121	$2.41 \cdot 10^{-4}$	15.4	8.71	1.31
116	5.12	15.1	8.16	1.26
61	$3.22 \cdot 10^{-3}$	15.3	8.69	1.32

Mean $1.30 \cdot 10^{-3}$ mm.

Determination of the Vapour Pressures of Cesium and Rubidium.

The arrangement of the apparatus was that shown in fig. 1. The fibre manometer was supported by two clamps

Fig. 1.



at C and D attached to a vertical iron support about 2 feet high. This support was rigidly fixed at the bottom to a stone table and at the top by an iron bracket to the wall. The manometer was surrounded by an air-bath consisting of an iron tube 5 cm. in diameter, wrapped with asbestos, and

heated electrically. The bath was kept at a temperature of approximately 150°C ., determined by means of a mercury thermometer graduated in half-degrees. As this temperature only occurs in the correction formula $p = p' \sqrt{\frac{\theta'}{\theta}}$

a small error in its determination would not be serious.

The metal was contained in the bottom of the branch tube in the middle, connected to the gauge by tubing of $\cdot 8$ cm. internal diameter. This connecting tube was covered with a thin layer of asbestos, wound with nichrome wire and then lagged with more asbestos. By passing a current through the wire the connecting tube was also kept at a temperature of about 150° , so that the tube in the thermostat was the coldest part of the apparatus.

Before the cesium was distilled into this branch tube and before the charcoal bulb was attached to its side tube, the manometer was calibrated at 150° in this air-bath, and not touched until the conclusion of the experiment. After calibration the charcoal bulb was attached and the cesium introduced through the side tube (E) by a series of five successive distillations. A small tube containing about $\cdot 5$ c.c. of the metal was cooled in liquid air, the capillary end of it was broken and the tube passed quickly inside a wider tube (also cooled)—connected by a series of bulbs to the branch tube (E). The tube containing the cesium was sealed up and the apparatus evacuated. With the pumps running the metal was distilled out into the surrounding tube and then slowly from bulb to bulb, in order to get rid of as much of the adsorbed gas as possible. Each distillation occupied about three-quarters of an hour, and each bulb was sealed off and removed as soon as the metal had been expelled from it. There was a slight residue left after the first and second distillations, but none after the subsequent ones. During the process the trap between this part of the apparatus and the McLeod gauge and pumps was kept in liquid air in order to prevent any mercury vapour getting through to the cesium or rubidium. When the metal had been distilled into the branch tube and the side tube sealed off, the capillary at F was sealed up. The apparatus was left some hours in case the metal gave up any more gas, after which the charcoal bulb was put in liquid air and the capillary at G sealed up. In both cases the capillaries F and G were just closed and not detached in order that the gauge supports might be as nearly identical as possible during the experiment and during the calibration.

In order to determine how much residual gas was left in

the apparatus the branch tube containing the metal was placed in a mixture of CO_2 snow and ether. This reduced the vapour pressure practically to nil, and a reading of the manometer was taken. This was also done at the conclusion of the experiment and the mean value taken as the residual gas pressure during the experiment.

The branch tube was now placed in a thermostat and readings of the gauge taken at various temperatures. It was found impossible to use any thermostat in which a stirrer was employed, as the motion of the fluid affected the vibration of the fibre. In consequence a small mercury thermostat was constructed. A glass tube (4×11 cm.) surrounded by an electric heater, contained the mercury, and the whole was well lagged. A small coil of enamelled nichrome wire actually in the mercury supplied a fine adjustment. The subsidiary current was switched on and off by means of a relay connected to a mercury thermometer with a large bulb. The coil was supported on a spiral of thick iron wire at a distance of about 2 mm. from the bulb of the controlling thermometer. With a current of 4 amp. the period of the relay was from 20 to 30 seconds, and the temperature was kept constant to $\pm 1^\circ \text{C}$. In spite of the lagging, however, there were variations in the temperature of the mercury in different parts of the thermostat, the extreme readings differing by $\pm 1.5^\circ$. The temperature was therefore known to $\pm 2.5^\circ$.

The procedure in the case of rubidium was exactly the same as for caesium.

Before the commencement of the experiment the calibration of the gauge was checked and found to be correct.

RESULTS.

Vapour Pressure of Caesium.

Equation (1) becomes

$$1.863 = T(11.52 p_{\text{Cs}} + \Sigma p M^{1/2} + 3.361 \cdot 10^{-3}),$$

where p_{Cs} is the vapour pressure of caesium and $\Sigma p M^{1/2}$ is the residual gas term.

Initial residual gas pressure.

$$T = 384. \quad 1.863 = 384(\Sigma p M^{1/2} + 3.361 \cdot 10^{-3}).$$

$$\therefore \Sigma p M^{1/2} = 1.491 \cdot 10^{-3}.$$

Final residual gas pressure

$$T = 377.8, \text{ whence } \Sigma pM^{1/2} = 1.571 \cdot 10^{-3}.$$

$$\text{Mean value } 1.531 \cdot 10^{-3}.$$

Therefore we have for the determination of the vapour pressure of caesium the equation

$$\begin{aligned} 1.863 &= T(11.52 p_{Cs} + 1.531 \cdot 10^{-3} + 3.361 \cdot 10^{-3}) \\ &= T(11.52 p_{Cs} + 4.894 \cdot 10^{-3}). \end{aligned}$$

The value of p_{Cs} given in the second column, Table III., corresponds to the pressure of the vapour in the gauge which is at a temperature of about 150° . We get the true value of

the vapour pressure from this by multiplying by $\sqrt{\frac{\theta}{\theta'}}$,

where θ is the temperature of the thermostat and θ' the temperature of the fibre manometer.

In the case of rubidium the initial and final values of $\Sigma pM^{1/2}$ were $1.213 \cdot 10^{-3}$ and $1.559 \cdot 10^{-3}$. The equation for determining the vapour pressure becomes therefore

$$1.863 = T(9.244 p + 4.747 \cdot 10^{-3}).$$

The results are given in Table IV.

Calculation of Chemical Constants.

The graph shows the observed values of $\log p$ plotted against $\frac{1}{T}$ absolute. For comparison the values of $\log p$ at higher temperatures obtained by Hackspill ('Recherches sur les Métaux Alcalins,' p. 65: Paris, Gauthier Villars), are also shown.

The points lie very closely on two straight lines—showing that the specific heats of the liquid metals are practically constant over the range considered. As the observations were made at comparatively low temperatures it was deemed justifiable to extrapolate linearly to find the vapour pressure at the melting-point and hence the chemical constants of the two metals.

TABLE III.—Vapour Pressure of Cæsium.

T (seconds).	p (mm. of Hg).	θ Abs.	θ' Abs.	$p' (= p \sqrt{\frac{\theta}{\theta'}})$	$\log p'$	$\log p'$ Calc.	Error.
1	$4.43 \cdot 10^{-3}$	321.4	424.5	$3.85 \cdot 10^{-3}$	-4.4145	-4.421	+0065
2	8.01	330	424.3	7.07	-4.1506	-4.117	+0336
3	$2.04 \cdot 10^{-4}$	341.1	424.3	$1.83 \cdot 10^{-4}$	-3.7375	-3.746	+0085
4	3.40	348.5	424.0	3.08	-3.5114	-3.513	+0016
5	4.71	352.5	423.5	4.30	-3.3665	-3.3391	+0245
6	8.49	362.2	423.5	7.86	-3.1046	-3.106	+0014
7	$1.93 \cdot 10^{-3}$	374.0	423.8	$1.81 \cdot 10^{-3}$	-2.7423	-2.779	+0367
8	3.38	386.6	424.0	3.23	-2.4908	-2.452	+0388

TABLE IV.—Vapour Pressure of Rubidium.

T (seconds).	p (mm. of Hg).	θ Abs.	θ' Abs.	$p' (= p \sqrt{\frac{\theta}{\theta'}})$	$\log p'$	$\log p'$ Calc.	Error.
1	$5.20 \cdot 10^{-5}$	264.5	424.2	$5.61 \cdot 10^{-5}$	-4.2510	-4.2162	+0348
2	$1.025 \cdot 10^{-4}$	371.3	426.1	$1.10 \cdot 10^{-4}$	-3.9586	-4.0046	+0460
3	1.59	378.0	426.0	1.69	-3.7721	-3.8037	+0316
4	2.13	384.7	424.8	2.24	-3.6498	-3.6098	+0400
5	2.86	388.1	425.2	3.00	-3.5229	-3.5139	+0090
6	4.86	395.2	425.5	5.04	-3.2976	-3.3191	+0215
7	5.31	397.8	426.3	5.50	-3.2596	-3.2494	+0101
8	6.25	400.0	426.3	6.45	-3.1904	-3.1913	+0009

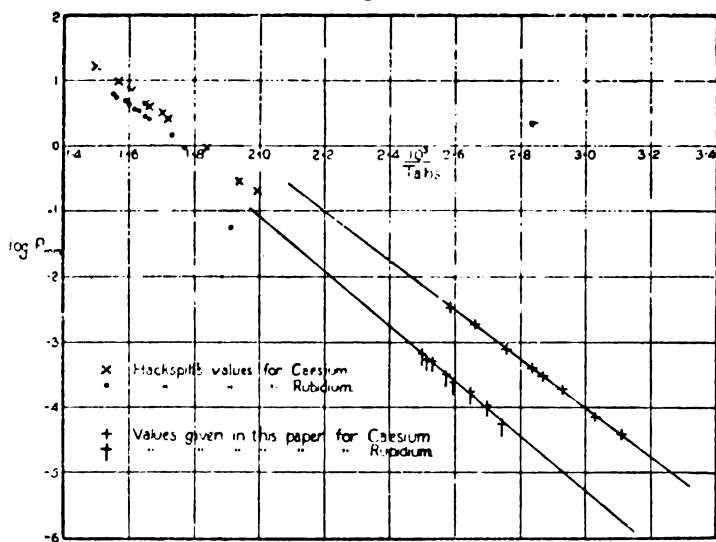
Assuming that $\log p = k - \frac{a}{T}$, the most probable values of k and a can be worked out—giving for cæsium

$$\log p = 7.256 - \frac{3753}{T},$$

and for rubidium

$$\log p = 7.331 - \frac{4209}{T}.$$

Fig. 2.



The values of $\log p$ calculated on this formula for the various values of T are given in the sixth column in the Tables III. and IV., and the differences between them and the observed value in the last column.

The method employed in the calculation of the chemical constants is similar to that developed by Egerton (Phil. Mag. Jan. 1920, p. 1).

We have from the Clausius-Clapeyron relation

$$\log_e p = -\frac{\lambda_0}{RT} + \int_0^T \frac{dT}{RT^2} \int_0^T (C_p - c_p) dT + i,$$

where C_p = atomic heat of vapour,

c_p = atomic heat of solid,

λ_0 = molecular latent heat at absolute zero.

In Egerton's paper it is shown that for the purposes of integrating the second term on the right-hand side of this equation, it is sufficiently accurate to put $c_p = c_r + \alpha T^{3/2}$, where α is a constant.

If we take $c_p = c_r + \alpha T^{3/2}$ and $C_p = \text{const} = 4.963$ and transform the logarithms to the base 10, we get

$$\log p = - \frac{\lambda_0}{4.571 T} + 2.5 \log T - \frac{1}{4.571 T} F - 0.0583 \alpha T^{3/2} + C, \quad \dots (3)$$

where $F = T \int_0^T \frac{1}{T^2} \int_0^T c_r dT$, and C is the chemical constant.

Also for the molecular latent heat at the melting-point we have

$$\lambda_T = \lambda_0 + \int_0^T (C_p - c_p) dT - f_m,$$

where f_m = latent heat of fusion at melting-point.

Substituting for C_p and c_p , as before, we find

$$\lambda_0 = \lambda_T - 4.963 T + E + f_m + \frac{2}{5} \alpha T^{5/2}, \quad \dots (4)$$

where $E = \int_0^T C_r dT$.

The values of $\frac{E}{T}$ and $\frac{F}{T}$ on Debye's formula for various values of $\frac{\beta\nu}{T}$ are tabulated in Nernst's 'Die Theoretischen und Experimentellen Grundlagen des Neuen Warmesatzes.'

Certain difficulty attends the determinations of the value of $\beta\nu$ for caesium and rubidium, and until figures are available which give the accurate values of the specific heats of these metals at low temperatures it will not be possible to calculate the chemical constant with accuracy from the vapour pressure measurements given in this paper.

The only values available are those given by Dewar (P. R. S. lxxxix. p. 158 (1913)), who found that at 50° Abs. $C_p = 6.05$ for rubidium and 6.82 for caesium. Using the correction formula $c_p = c_r + c_p^2 \frac{T}{T_s} A_0$ the corresponding values of C_r are found to be 5.92 and 6.65 respectively.

The value 6.65 is of no use since it is greater than 3R and the value 5.92 gives a value for $\beta\nu$ for rubidium about

a fifth of that obtained from the Lindemann melting-point formula. The probable explanation that these values of the atomic heat are so much higher than one would expect is that the metal still contained an appreciable quantity of hydrogen or other impurity at the time of the experiment.

Measurements have been made, however, on the Atomic Heat of Sodium at Low Temperatures (E. H. Griffiths & Ezer Griffith, *Phil. Trans.* cxiv. p. 348 (1914), and Günther, *Annalen der Physik*, lxiii. p. 476 (1920)). If the value of $\beta\nu$ for sodium is calculated from these measurements we can work out the constant k in the Lindemann melting-point formula

$$\nu = k \sqrt{\frac{T_s}{m r^2}}$$

and then work back to the values of $\beta\nu$ for caesium and rubidium. This should give a fairly accurate value, for if the constant is suitably chosen the formula holds tolerably well for members of the same group of elements. Unfortunately there is a serious discrepancy between the two series of observations. The value of the constant k corresponding to Griffith's value of $\beta\nu$ for sodium is $2.6 \cdot 10^{12}$, while that corresponding to Günther's value is $2.0 \cdot 10^{12}$. In view of this discrepancy and the absence of any data for caesium and rubidium themselves, the values of $\beta\nu$ used in the following calculations of the chemical constants were obtained by using in the melting-point formula the constant $2.8 \cdot 10^{12}$ —which is the value giving the best results when all the elements are considered.

The specific heats of both caesium and rubidium have been measured at room temperature and can be used to determine “ a ” in the correction formula $C_p = C_v + aT^{3/2}$.

The values of f_m , the molecular latent heats of fusion, are given by Rengarde (*Comptes Rendus*, clvi. p. 1897 (1913)).

Chemical Constant of Caesium.

$$\beta\nu = 49.5. \quad T_m = 301.25.$$

From the vapour measurements in this paper

$$\log p = 7.256 - 3753/T.$$

$$\text{At the melting-point } \lambda_{T_m} = RT_m^2 \frac{d}{dT}(\log p) = 17155,$$

$$4.963 T_m = 1496.$$

At 0°C , $C_p = 6.396$,

$$\frac{\beta\nu}{T} = 0.181, \quad \therefore C_v = 5.94,$$

$$\text{but } C_p = C_v + aT^{3.2}.$$

$$\therefore a = 8.72 \cdot 10^{-5}.$$

At the melting-point $\frac{\beta\nu}{T_m} = 0.164$, $\therefore \frac{E}{T} = 5.596$,

$$\text{and } E = 1686.$$

$$4aT^{5.2} = 55,$$

$$f_m = 500.$$

Substituting in equation (4) we get $\lambda_0 = 17895$.

At the melting-point we have $\frac{\lambda_0}{RT_m} = 12.995$,

$$2.5 \log T_m = 6.192,$$

$$\frac{F}{T} = 13.25, \quad \frac{F}{RT} = 2.898,$$

$$\log p = 7.256 - 3753/T = -5.202 \text{ mm.} = -8.032 \text{ atmospheres.}$$

$$0.583 aT^{3.2} = 0.27.$$

In working out the probable error of the result it is assumed that T_m is known to 0.1° and that the latent heat of fusion per gramme is known to 0.1 calorie. The probable errors of λ_{T_m} and $\log p_m$ are worked out from the errors in column 8, Table III., and therefore take into account the probable error in the observation of the temperature of the thermostat. An error of 5 per cent. is allowed for in the determination of $\beta\nu$ from the melting-point formula.

Substituting in equation (3) we now have

$$12.995 \pm 0.077 \qquad 6.198 \pm 0.001$$

$$2.898 \pm 0.068 \qquad 8.082 \pm 0.018$$

$$0.27$$

$$15.920 \pm 0.145 \qquad 14.280 \pm 0.019$$

$$14.280 \pm 0.019$$

$$C = \underline{1.640 \pm 0.164}$$

Chemical Constant of Rubidium.

$$\beta\nu = 68\cdot1. \quad T_m = 311\cdot5.$$

From the vapour pressure measurements

$$\log p = 7\cdot331 - 4209/T.$$

At the melting-point $\lambda_{T_m} = 19239$,

$$4\cdot963 T_m = 1545,$$

$$\frac{\beta\nu}{T} = 0\cdot219, \quad \text{whence} \quad E = 1708.$$

$$\text{At } 0^\circ \text{C.} \quad C_p = 6\cdot85, \quad \frac{\beta\nu}{T} = 0\cdot249. \quad \therefore C_v = 5\cdot94$$

$$a = 2\cdot01 \cdot 10^{-4},$$

$$\cdot4 a T^{5\cdot2} = 138,$$

$$f_m = 525,$$

$$\therefore \text{from equation (4)} \quad \lambda_0 = 26054.$$

$$\text{At the melting-point} \quad \frac{\lambda_0}{RT_m} = 14\cdot084,$$

$$2\cdot5 \log T_m = 6\cdot234,$$

$$\frac{F}{T} = 11\cdot52, \quad \therefore \frac{F}{RT} = 2\cdot520,$$

$$\cdot0583 a T^{3\cdot2} = \cdot058,$$

$$\log p = 7\cdot331 - 4209/T = -6\cdot181 \text{ mm.} = -9\cdot062 \text{ atmospheres.}$$

Working out the probable errors of each term in the same way as for the caesium and substituting in equation (3) we have

$$14\cdot084 \pm \cdot098$$

$$9\cdot062 \pm \cdot024$$

$$2\cdot520 \pm \cdot061$$

$$6\cdot234 \pm \cdot001$$

$$\cdot058$$

$$16\cdot662 \pm \cdot159$$

$$15\cdot296 \pm \cdot025$$

$$15\cdot296 \pm \cdot025$$

$$C = \underline{1\cdot366 \pm \cdot184}$$

If $C = 1\cdot5 \log M + C_0$, where M is the molecular weight, the corresponding values of the absolute constant C_0 are $-1\cdot545 \pm \cdot164$ and $-1\cdot532 \pm \cdot184$. The value calculated

from the constants h and k is -1.608 , so that the results are in agreement within the error.

The equation $\log p = k - \frac{a}{T}$ obtained from the vapour pressure measurements may also be used to give an approximation by a rather long extrapolation to the value of λ at the boiling-point, from which Trouton's coefficient $\frac{\lambda_{T_B}}{T_B}$ (where T_B is the boiling-point) can be determined. The values obtained are 18.2 for caesium and 19.9 for rubidium.

Discussion of Results.

As the results for the chemical constants of both metals are both higher than the theoretical value by roughly the same amount, it seems probable that there is some other source of error not yet considered.

The true values of $\beta\nu$ may possibly be higher than those used in the above calculation, or if they are taken as correct the high values of the chemical constant suggest that the individual measurements of the vapour pressures are also all too high.

This may be due to two causes :

(1) The caesium or rubidium might have given up an appreciable quantity of gas after the apparatus was finally sealed off, and re-absorbed a certain amount of it each time it was cooled in CO_2 snow and ether. The pressure of hydrogen required to produce an increase of $.07$ in the chemical constant is of the order 10^{-3} mm. in excess of that given by the "residual gas pressure" determinations ; and a correspondingly smaller amount of any other gas of larger molecular weight would produce the same effect.

(2) The trap immersed in liquid air might have allowed a certain amount of mercury vapour to pass through during calibration. This would have made the observed times T too small and in consequence the calculated value of the constant b in equation (1) would be too large. Pressures re-calculated from the formula would therefore also be too large.

In order to test the efficiency of the trap the following experiment was carried out. The fibre manometer, calibrated in the usual way with the trap in liquid air, was used to measure the amount of mercury vapour passing through the trap when it was cooled in CO_2 snow and ether instead of in liquid air. Two series of readings were taken, one with the trap empty, the other when it was filled with copper

turnings, in order to increase the cold surface exposed to the gas. The trap was found to be somewhat more efficient when full of copper turnings than when empty. A third series of readings were taken with the trap full of copper turnings immersed in liquid air. This series was found to be in complete accord with the calibration readings, which means that the trap, if immersed in liquid air, stops as much mercury vapour when it is empty as when it is full of copper turnings. This shows that the trap may be regarded as perfectly efficient when immersed in liquid air.

It seems unlikely that the metal should give up so much gas after the care taken over its distillation into the apparatus, and therefore the probable source of the error is the uncertainty of the value of $\beta\nu$.

The actual amounts of mercury vapour which passed through the trap when it was immersed in CO_2 snow and ether were surprisingly large, and it is therefore thought desirable to give the results of the experiment in detail.

Two traps of the shape shown in fig. 1 were used. The dimensions were as follows:—

	Trap I.	Trap II.
Internal diameter of outside tube	2 cm.	1·8 cm.
" " " inside "	·9 cm.	·8 cm.
Height between bottom of inside tube and surface of cooling liquid	12·3 cm.	11·2 cm.

Trap I. was, unfortunately, broken after the 1st series of readings, before it was filled with copper turnings. The results are, however, given because they agree remarkably well with those obtained from Trap II. when empty, although the dimensions of the traps are different.

The fibre manometer employed was the same as that used for the determination of the vapour pressures of cæsium and rubidium. It was re-calibrated at room temperature in the ordinary way with the trap in liquid air. The values found for the constants a and b in equation (1) were

$$b = 1\cdot780,$$

$$a = 3\cdot116 \cdot 10^{-3}.$$

The values at 150°C. were

$$b = 1\cdot863,$$

$$a = 3\cdot361 \cdot 10^{-3},$$

showing that the constants change slightly with the temperature.

The results for the various series of readings are given in Tables V., VI., and VII.

TABLE V.

Amount of Mercury Vapour let through by Trap I., empty.

T, seconds.	p , air pressure.	π , pressure of mercury vapour.
82.7	$3.02 \cdot 10^{-3}$	$1.52 \cdot 10^{-4}$
118	1.59	2.39
131	1.38	2.17
156	1.09	1.71
176.3	.884	1.56
222	.405	1.94
300.7	.047	1.78

Mean $1.87 \cdot 10^{-4}$

TABLE VI.

Amount of Mercury Vapour let through by Trap II., empty.

T, seconds.	p , air pressure.	π , pressure of mercury vapour.
75.7	$3.32 \cdot 10^{-3}$	$1.78 \cdot 10^{-4}$
111	1.91	1.86
120	1.72	1.74
162	.97	1.86
174	.87	1.71
289	$< 10^{-5}$	2.12

Mean $1.84 \cdot 10^{-4}$

TABLE VII.

Amount of Mercury Vapour let through by Trap II.
when filled with Copper Turnings.

T, seconds.	p , air pressure.	π , pressure of mercury vapour.
70.0	$3.79 \cdot 10^{-3}$	$1.36 \cdot 10^{-4}$
127	1.73	1.14
152	1.28	1.21
176	1.02	1.06
204	.77	.98
214	.63	1.49
277	.33	1.06
380	$< 10^{-5}$	1.10

Mean $1.17 \cdot 10^{-4}$

It will be seen that the trap, when cooled in CO₂ snow and ether, lets through an amount of mercury vapour which is roughly constant for air pressures from $5 \cdot 10^{-3}$ mm. downwards. The mean values for Traps I. and II. empty are $1 \cdot 87 \cdot 10^{-4}$ and $1 \cdot 8 \cdot 10^{-4}$ mm. respectively, and for Trap II. full of copper turnings $1 \cdot 17 \cdot 10^{-4}$ mm.

The experiment was conducted at room temperature (about 14° C.), and as the vapour pressure of mercury at this temperature is about $8 \cdot 10^{-4}$, the figures show that the trap allows mercury to pass through up to 23 per cent. of the vapour pressure when it is empty and up to 15 per cent. when it is full of copper turnings.

SUMMARY.

(1) A slightly modified form of Haber's vibrating quartz fibre manometer is described.

(2) The vapour pressure of mercury is measured at room temperature. The mean of the results, corrected to 20° C., is $1 \cdot 30 \cdot 10^{-3}$ mm.

(3) The vapour pressures of cæsium and rubidium at various temperatures between 50° C. and 130° C. are measured. The relation between $\log p$ and $1/T$ is found to be approximately linear over the range considered, and the results can be represented by the formulæ

$$\log p = 7 \cdot 256 - 3753/T \quad \text{for cæsium,}$$

$$\text{and} \quad \log p = 7 \cdot 331 - 4209/T \quad \text{for rubidium.}$$

(4) The chemical constants of the two metals are calculated; the values obtained are $1 \cdot 64(0) \pm \cdot 16(4)$ for cæsium and $1 \cdot 36(6) \pm \cdot 18(4)$ for rubidium. If $C = 1 \cdot 5 \log M + C_0$, where M is the molecular weight, the values obtained for the absolute chemical constant C_0 are $-1 \cdot 54(5) \pm \cdot 16(4)$ and $-1 \cdot 53(2) \pm \cdot 18(4)$. The theoretical value of C_0 is $-1 \cdot 608$, so that the results are in agreement within the error.

(5) The value of Trouton's coefficient $\frac{\lambda_{TB}}{T_B}$ (where T_B is the boiling-point) is worked out; giving 18.2 for cæsium and 19.9 for rubidium.

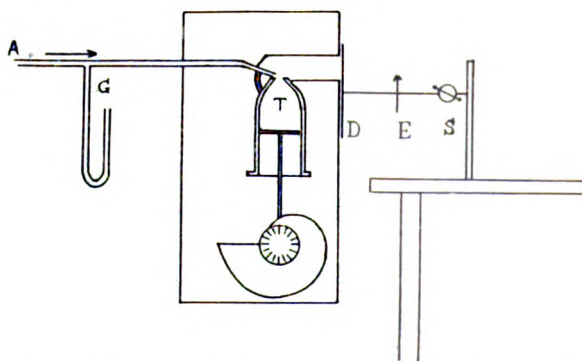
(6) The chemical constants for both metals are above the theoretical value. The possible reasons for this are discussed.

(7) Some measurements are made on the amount of mercury vapour passing through a trap of the ordinary type when cooled in CO_2 snow and ether. The mean value is found to be $1.84 \cdot 10^{-4}$ mm. It is shown that the trap is more efficient when filled with copper turnings; the mean value in this case being $1.17 \cdot 10^{-4}$. When the trap is cooled in liquid air the readings with and without copper turnings in the trap are in complete agreement.

IV. *On the Critical Frequency of Pulsation of Tones.* By MOLLIE WEINBERG, M.A., M.Sc., Research Student of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, and FRANK ALLEN, Ph.D., F.R.S.C., Professor of Physics, University of Manitoba*.

THE successful application of the principle of the persistence of vision, or the critical frequency of flicker, to the study of problems of colour vision suggested the probable value of the analogous principle of the persistence of audition to the solution of problems of the perception of sound. In this communication the results of some investigations based on this latter principle are described, which show that the method is capable of extension to some of the phenomena of physiological acoustics.

Fig. 1.



The experimental arrangements, fig. 1, were similar to those used in investigations in Colour Vision†.

* Communicated by the Authors. Read at the meeting of the Royal Society of Canada, Ottawa, May 1922.

† Phys. Rev. vol. xi. p. 257 (1900); Phil. Mag. vol. xxxviii. p. 55 (1919).

The source of sound was a Stern Tonvariator, T, placed inside a box lined with very soft thick felt, through which at a suitable place a hole was cut. The tonvariator was blown by a stream of air from a large constant-pressure tank, and the pressure was further regulated by suitable cocks, and measured by a small water-gauge, G. The periodic interruption of the continuous sound into separate pulses was effected by the rotation of a light aluminium disk, D, with four symmetrically placed holes of the same size as that in the box. For this purpose an electric motor was used, which was connected with a storage battery to secure exact regulation of the speed. A speed counter, S, making electric contact every fiftieth revolution of the disk, and a clock beating half seconds, were connected with a chronograph from which the speed of the disk, and hence the critical frequency of pulsation, or flutter, of the sound was computed when it became just continuous to the ear.

The ideal disk should completely interrupt the sound ray except when its openings coincide with that in the box from which the sound is issuing. To secure this, the disk might be made of the most inelastic material possible. But it is also essential that it should be very light, to permit rapid adjustment for the critical frequency of pulsation, or flutter, of the sound. A thin aluminium disk was chosen, as stated above, which was covered with velvet to dampen the vibrations as far as possible. The velvet served another purpose also, since the disk could be placed so close to the box that the velvet pile just grazed its surface. It is remarkable how greatly the intensity of the sound escaping between the box and the disk is lowered by eliminating the last slight distance between them. The ear of the observer—in this arrangement of apparatus the left was most conveniently used—was always placed in the same position, E, so that variations in the intensity of sound could not be attributed to any condition other than the rotation of the disk.

The tonvariator* is a simple König resonator with a movable bottom acting like a piston. To regulate the pitch of the tone, the piston is moved by a pin resting on the edge of a brass plate cut in a spiral of such a form that the frequencies may be read directly on an evenly-graduated circular disk rigidly attached to the spiral. The tonvariator was capable of giving pure tones of considerable variation in intensity covering the octave from 150 to 300 double vibrations per second. Since the frequencies of the tonvariator varied with

* *Physikalische Zeitschrift*, vol. v. p. 693 (1904).

the blowing pressure, it became necessary to obtain calibration curves from standard tuning forks. These curves were exact straight lines. The corrected frequencies ranged from 142 to 285 vibrations. The intensities were those obtained with air-pressures from 1.25 to 2.40 cm. of water. Above and below these pressures the tones were not sufficiently pure for experimental purposes.

The greatest care was taken to eliminate all extraneous noises in motor, disk, and chronograph. But it was found impossible with such arrangements as were available at the time to prevent some sound escaping from the surface of the box and through the disk. The rotation of the disk produced marked variation of the intensity of the sound ray, but the ideal sudden transition from silence to full intensity, as from darkness to light, was by no means realized. No doubt great improvements are possible in the control of sound, which we have found the most difficult part of the problem.

In making the measurements the tonvariator was adjusted to give a steady sound of the desired pitch and intensity. The ear was then placed at the proper place and the speed of the disk increased so that the interrupted pulses of sound became fused into a just continuous sensation. The chronograph circuits were then closed and the readings recorded. Each record gave several measurements, from which mean values of the critical frequency of pulsation were obtained. Each point on the curves is the mean of about ten measurements obtained from three or four independent determinations.

For each pressure or intensity of sound such measurements were made for seven frequencies extending through the octave. Ten pressures also were used between the limits mentioned above. These measurements are recorded in Table I., from which the corresponding normal curves are plotted in fig. 2. Each normal curve represents the relation between the vibration frequency, N , and the duration of the tone at the critical frequency of pulsation, D , for the octave mentioned, at a definite pressure or intensity of sound, P , when the ear was in its normal unfatigued condition. The ten normals form a regular family of curves, all being slightly convex toward the axis of frequencies.

The lowest curve of the group is that obtained with the least pressure or intensity of sound, and the highest with the greatest pressure or intensity. It has been shown by Love and Dawson* that the intensity of sound emitted by a

* Phys. Rev. vol. iv. p. 49 (1919).

TABLE I.

Normal Curves Corrected for Frequency.

N.	D.	P.	N.	D.	P.
A. 142.0	0.0185	1.25 cm.	F. 143.0	0.0206	1.82 cm.
164.0	0.0172	"	167.0	0.0192	"
186.0	0.0160	"	190.0	0.0182	"
208.0	0.0149	"	214.0	0.0170	"
230.0	0.0139	"	237.0	0.0161	"
252.0	0.0130	"	260.5	0.0153	"
264.0	0.0127	"	284.0	0.0146	"
B. 142.5	0.0194	1.45 cm.	G. 143.0	0.0210	1.98 cm.
165.5	0.0181	"	167.0	0.0195	"
187.5	0.0168	"	190.0	0.0184	"
210.0	0.0157	"	214.0	0.0173	"
235.0	0.0146	"	237.0	0.0163	"
256.7	0.0137	"	260.5	0.0154	"
278.0	0.0130	"	284.0	0.0148	"
C. 142.8	0.0197	1.53 cm.	H. 143.0	0.0211	2.10 cm.
165.8	0.0184	"	167.2	0.0200	"
188.8	0.0172	"	190.2	0.0187	"
211.8	0.0161	"	214.2	0.0177	"
235.7	0.0152	"	237.2	0.0166	"
257.9	0.0143	"	260.7	0.0158	"
280.5	0.0138	"	284.2	0.0151	"
D. 142.9	0.0201	1.62 cm.	I. 143.2	0.0212	2.20 cm.
166.2	0.0187	"	167.3	0.0203	"
189.0	0.0177	"	191.0	0.0190	"
212.0	0.0166	"	214.6	0.0180	"
235.3	0.0155	"	238.0	0.0171	"
258.2	0.0146	"	261.2	0.0160	"
280.9	0.0140	"	284.2	0.0155	"
E. 143.0	0.0203	1.70 cm.	J. 143.5	0.0215	2.40 cm.
166.6	0.0190	"	168.2	0.0205	"
189.7	0.0179	"	191.2	0.0192	"
213.2	0.0168	"	215.0	0.0184	"
236.2	0.0158	"	238.3	0.0173	"
259.3	0.0149	"	261.9	0.0163	"
283.0	0.0143	"	285.0	0.0156	"

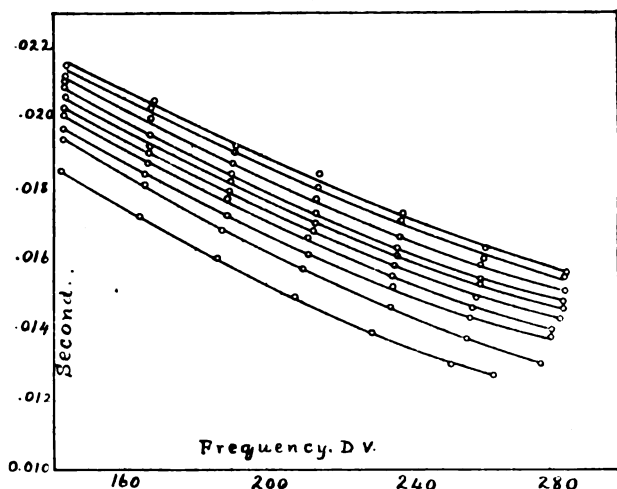
resonator is proportional to the blowing pressure. Assuming this to be true for the form of resonator used in this investigation, the curves in fig. 2 may be regarded as indicating definitely the relation between the vibration frequency, the duration of the tone at the critical frequency of pulsation, and the intensity of the tone.

It is worthy of remark that in the analogous normal persistency curves for spectra* of varying intensities the opposite condition prevails. With light the brightest colours give the lowest curve, that is, they have the smallest values

* Phil. Mag. vol. xxxviii. p. 81 (1919).

of the duration of the light at the critical frequency of flicker; whereas in sound the greatest intensities have the largest values of the duration of the tone at the critical frequency of pulsation. The mechanisms in the two sets of phenomena are widely different. Vision probably results from photo-electric action on the nerves; in sound the auditory nerves are excited by mechanical vibrations.

Fig. 2.



A somewhat similar investigation to that described above was made by Mayer*. His method was as follows: between a vibrating tuning fork and its resonator he interposed a revolving disk with openings of the same shape as that in the resonator, so that the sound was heard loudly when an opening in the disk came in front of that in the resonator, and faintly when the latter was covered. He found that his measurements conformed to the law

$$D = \frac{K}{N} + C,$$

where D is the duration of the tone at the critical frequency of pulsation, N the frequency of the fork, and K and C are constants.

The measurements given in Table I. were tested by this law and found, when plotted, not to give straight lines.

* *Philosophical Magazine*, ser. 3, vol. viii. (1874); Helmholtz, 'Sensations', p. 417.

The graphs possessed a slight regular curvature very similar to that of the normal curves in fig. 2, but opposite in sign. No doubt the time of duration of the sound at the critical frequency of pulsation and the frequency of the tone are connected in some inverse relation. The precise nature of that function, as will later be discussed, appears to be

$$D = \frac{K}{\sqrt{\log N}} + C$$

where the letters D , N , K , C have the same significance as above.

The difference between Mayer's relation and that here obtained is probably due to his method of interposing a resonator between the source of sound and the ear, whereas in our experiments the fusion of sounds was effected in the ear directly. Another possible explanation of Mayer's results is given in a later communication, "On the Effect of Aural Fatigue" *.

It will be noticed in fig. 2 that the vertical distances between the normal curves are not equal. The interval between the curves for the highest intensities is small, and gradually increases as the intensity is decreased. This suggested the possibility that some law connecting the duration time at the critical frequency of pulsation and the intensity of the sound might be deduced.

In colour vision, Ferry† and Porter‡ found that the relation between the duration, D , of a flash of colour upon the retina at the critical frequency of flicker and the luminosity, L , was expressed by the equation

$$D = \frac{1}{K \log L}, \quad \dots \quad (\text{Ferry})$$

$$\text{or} \quad n = K \log L + C \quad \dots \quad (\text{Porter})$$

where n is the reciprocal of D , and K and C are constants. This equation is independent of the wave-length of the light.

As we have seen, the intensities of sounds and their duration at the critical frequency of pulsation have a direct and not an inverse relationship, as is the case in colour vision. Several equations suggested by the above were tried without success.

* P. 126.

† Amer. Jour. Sci. (3), vol. xlv. p. 193 (1892).

‡ Proc. Roy. Soc. vol. lxx. p. 313 (1902).

That which appears to give the best result is

$$D = K \sqrt{\log P} + C$$

where D is the duration of the sound at the critical frequency of pulsation, P the blowing pressure to which the intensity of the sound is proportional, N the frequency of vibration of the tone, and K and C are constants.

In fig. 3, plotted from the values in Table II., the critical frequencies of pulsation are plotted against the square roots of the logarithms of the pressure. The resulting curves are, in all five cases, straight lines.

Fig. 3.

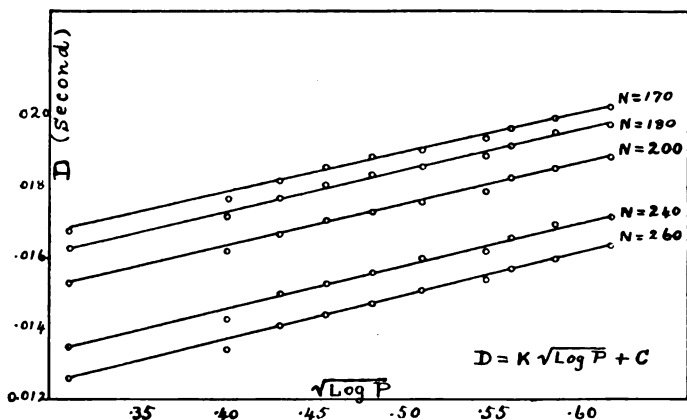


TABLE II.

Pressure P .	$\sqrt{\log P}$.	D . $N=170$. sec.	D . $N=180$. sec.	D . $N=200$. sec.	D . $N=240$. sec.	D . $N=264$. sec.
2.40 cm.	0.616	0.0203	0.0198	0.0189	0.0172	0.0164
2.20 "	.585	.0200	.0196	.0186	.0170	.0160
2.10 "	.560	.0197	.0192	.0183	.0166	.0157
1.98 "	.546	.0194	.0189	.0179	.0162	.0154
1.82 "	.510	.0191	.0186	.0176	.0160	.0151
1.70 "	.482	.0189	.0184	.0173	.0156	.0147
1.62 "	.456	.0186	.0181	.0171	.0153	.0144
1.53 "	.430	.0182	.0177	.0167	.0150	.0141
1.45 "	.401	.0177	.0172	.0162	.0143	.0134
1.25 "	.3311	.0168	.0163	.0153	.0135	.0126

A further test was made. The tonvariator was maintained constant at three different frequencies in succession, and the pressures adjusted for eight successive values in each case. The frequencies used were 170, 200, and 240 vibrations.

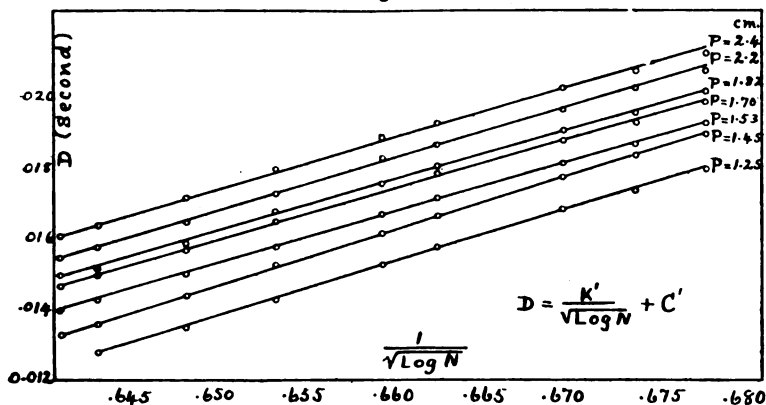
The data obtained are incorporated in Table II. with those for the same frequencies taken from the normal curves. The straight lines in fig. 3 are therefore the result, not only of data taken from the normal curves, but also of data obtained directly from independent measurements. This forms a more complete verification of the law that, at the critical frequency of pulsation, the duration of a pulse of sound varies directly as the square root of the logarithm of the pressure or intensity.

Further investigations were made concerning the relation between the critical frequency of pulsation, D , and the frequency of the tone, N , when the pressure remained constant. It will be remembered that Mayer had expressed that relation in the form

$$D = \frac{K}{N} + C.$$

On applying new data obtained in this investigation, the above law does not hold. The only manner in which Mayer's

Fig. 4.



equation agrees with data here obtained is in the fact that both indicate an inverse relationship. The precise nature of this inverse function was not at first apparent. After trying a number of equations, however, we find the one that appears to give the best results to be

$$D = \frac{K'}{\sqrt{\log N}} + C'$$

where D and N have same meaning as previously, and K' and C' are arbitrary constants. In fig. 4, plotted from the

data in Table III., the time values of the critical frequencies of pulsation are plotted against the reciprocals of the square roots of the logarithms of the frequencies, and again, the results are seen to be very consistent straight lines.

TABLE III.

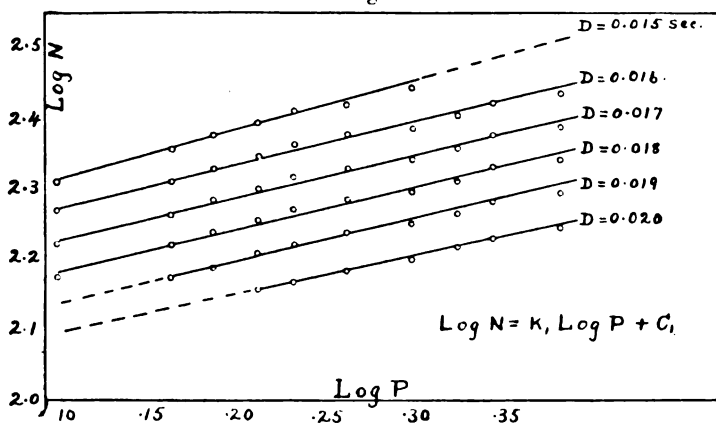
N.	$\frac{1}{\sqrt{\log N}}$	D.	D.	D.	D.	D.	D.	D.
		P= 2.40c. sec.	P= 2.10c. sec.	P= 1.82c. sec.	P= 1.70c. sec.	P= 1.53c. sec.	P= 1.45c. sec.	P= 1.25cm. sec.
150	0.6779	0.0213	0.0208	0.0202	0.0199	0.0193	0.0190	0.0180
160	.6739	.0208	.0203	.0196	.0194	.0187	.0184	.0174
170	.6698	.0203	.0197	.0191	.0189	.0182	.0177	.0168
190	.6627	.0193	.0187	.0181	.0179	.0172	.0167	.0158
200	.6596	.0189	.0183	.0176	.0173	.0167	.0162	.0153
220	.6536	.0180	.0173	.0168	.0165	.0158	.0153	.0143
240	.6485	.0172	.0166	.0160	.0156	.0150	.0143	.0135
260	.6435	.0164	.0158	.0152	.0150	.0143	.0136	.0128
270	.6414	.0161	.0155	.0150	.0147	.0140	.0133	...

It is very interesting to note that whereas D varies directly as the root of the logarithm of P when N remains constant, it varies inversely as the root of the logarithm of N when P remains constant. The square root of the logarithm seems to be involved in both relations.

This suggested the possibility of some simple relationship existing between N and P at a constant value of the frequency of pulsation, D . For this purpose, horizontal cross-sections were taken through the family of curves in fig. 2. Again, after many attempts had been made, the following equation seemed to give the best results:

$$\log N = K'' \log P + C'',$$

Fig. 5.



In fig. 5, values taken from Table IV., the logarithms of the frequencies were plotted against the logarithms of the

pressures. The resulting lines, although not as consistently straight as those representing the other relations, seem to verify the equation.

TABLE IV.

P.	Log P.	N.	Log N.	N.	Log N.	N.	Log N.
		D=0.0150 sec.		D=0.0160 sec.		D=0.0170 sec.	
1.25 cm.	0.0969	205	2.312	186	2.270	167	2.223
1.45 "	.1614	226	2.354	204	2.310	184	2.265
1.53 "	.1847	239	2.378	214	2.330	193	2.286
1.62 "	.2095	248	2.394	223	2.348	201	2.303
1.70 "	.2305	259	2.413	231	2.364	208	2.318
1.82 "	.2601	263	2.420	238	2.377	214	2.330
1.98 "	.2967	276	2.441	244	2.387	220	2.342
2.10 "	.3222	...	...	254	2.405	228	2.358
2.20 "	.3424	...	...	265	2.423	238	2.377
2.40 "	.3802	...	...	273	2.436	244	2.387
		D=0.0180 sec.		D=0.0190 sec.		D=0.0200 sec.	
1.25 cm.	0.0969	150	2.176	...	...	...	...
1.45 "	.1614	167	2.223	150	2.176	...	...
1.53 "	.1847	174	2.241	155	2.190	...	...
1.62 "	.2095	181	2.258	162	2.210	144	2.158
1.70 "	.2305	187	2.272	167	2.223	148	2.170
1.82 "	.2601	193	2.286	173	2.238	153	2.185
1.98 "	.2967	198	2.297	178	2.250	158	2.199
2.10 "	.3222	205	2.312	184	2.265	165	2.217
2.20 "	.3424	214	2.330	192	2.283	171	2.233
2.40 "	.3802	220	2.342	197	2.294	176	2.246

The three laws, therefore, which we have tentatively deduced are:—

$$D = K \sqrt{\log P} + C; \quad \dots \quad (1)$$

$$D = \frac{K'}{\sqrt{\log N}} + C'; \quad \dots \quad (2)$$

$$\log N = K'' \log P + C''. \quad \dots \quad (3)$$

Were it not that the C's in equations (1) and (2) are apparently different, the two equations might be put together in the form

$$D = K \frac{\sqrt{\log P}}{\sqrt{\log N}}.$$

This equation would define an acoustical surface, analogous in many respects to the well-known thermo-dynamic surface, each point on this acoustical surface denoting a relation between the pressure or intensity, the frequency of the tone, and its critical frequency of pulsation.

The above is an interesting conjecture, which might lead, on fuller investigation, to fruitful results.

The range of pressures and frequencies in this investigation was small, and before the above "laws" can be accepted with confidence they should be tested through a far greater range of intensities and frequencies than the apparatus used in this investigation afforded.

An attempt was made to determine whether normal measurements of other observers correspond with those here obtained, *i. e.*, whether the sensitivity to intensity and the duration of tones are the same for the average ear. Normal curves of four other observers have so far been obtained. These are shown in fig. 6, with the data from which they were plotted in Table V.

Fig. 6.

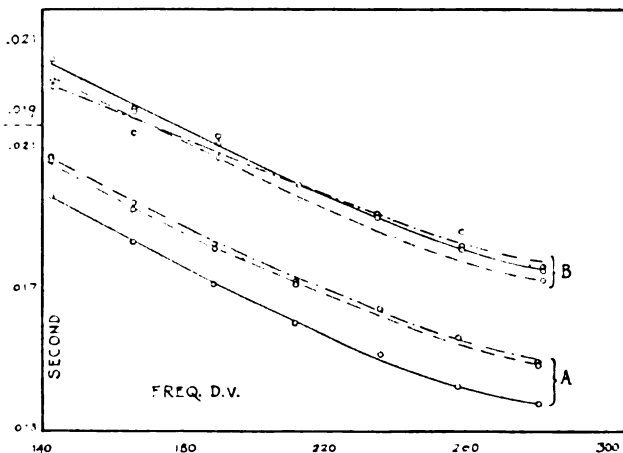


TABLE V.

Normal Curves of Other Observers.

A. N. D. (M.W.).	P.	P.	D. (E.W.).	P.	D. (H.W.).
Second.			Second.		Second.
142.8	0.0197	1.53 cm.	1.53 cm.	0.0207	1.53 cm.
165.8	.0184	"	"	.0193	"
188.8	.0172	"	"	.0182	"
211.8	.0161	"	"	.0172	"
235.7	.0152	"	"	.0165	"
257.9	.0143	"	"	.0157	"
280.5	.0138	"	"	.0149	"
B.	(M.W.).		(S.G.L.).		(A.H.).
143.0	0.0206	1.98 cm.	1.88 cm.	0.0200	1.90 cm.
166.0	.0192	"	"	.0185	"
190.0	.0182	"	"	.0178	"
213.0	.0170	"	"	.0165	"
236.0	.0161	"	"	.0162	"
259.0	.0153	"	"	.0152	"
282.0	.0146	"	"	.0143	"

The broken line and the dot-dash curves are those of the other observers ; the continuous curves are those of one of the authors (Weinberg) and are inserted for the sake of comparison. The data are also given in Table V.

The curves are divided into two groups ; those in group A were obtained at approximately the same pressure or intensity ; those in group B at different pressures or intensities.

The general slope of all the curves in both groups is very nearly the same. The very slight difference in curvature of the two curves in group B, as seen by their intersection at a very minute angle, may perhaps be attributed to the inexperience of the other observers.

Assuming the ears of all the observers to be average, this approximate sameness of the general slope may be taken to indicate that the degree of decrease in the duration of a tone, as its vibration frequency or pitch becomes higher, is very nearly the same for the average ear.

The relative vertical displacement of the curves in group A indicates that so-called normal ears are not equally sensitive to sounds of the same intensity, since the duration of tones of the same pitch at the critical frequency of pulsation differs.

In similar investigations in colour vision it was found that in persons between about eighteen and fifty-five years of age the sensitivity of normal eyes to the intensity of illumination is the same*. In audition, however, the sensitivity of the average ear to the intensity of tone varies. This difference is very probably due to the wide difference in the character of the two mechanisms or processes involved. The perception of light is most probably a photo-electric or chemical effect—a reaction of atoms and molecules to the stimulation of light-waves. Hence it is to be expected that for a constant intensity of stimulation there would be approximately constant atomic interactions, *i. e.*, approximately constant sensitivity. In the case of audition, however, the instrument of tone perception, the ear, is an extremely complicated mechanical structure, and therefore subject to many sources of defect or of difference. And in a mechanism so minute and delicate as the ear, it would be little less than miraculous were the mass, elasticity, and other physical properties of its component parts found always to be the same†.

* Ferry, *Am. Journ. Sci.* vol. xliv. (1892).

† Seashore, 'Psychology of Musical Talent,' p. 81.

We desire to express our thanks to Prof. J. C. McLennan, F.R.S., of Toronto University, for the loan of Standard König Tuning Forks used for calibration of the tonvariator.

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V. Tables of Bessel Functions. By HUGH E. H. WRINCH, M.I.Mech.E., and DOROTHY WRINCH, D.Sc., Fellow of Girton College, Cambridge, and Member of the Research Staff, University College, London*.

THE present paper contains further tables of the Bessel Functions.

The Bessel Functions† $J_n(x)$ and $I_n(x)$ may be defined for integer values of n by

$$J_n(x) = \frac{x^n}{2^n \Gamma(n+1)} \left\{ 1 - \frac{(x/2)^2}{1!(1+n)} + \frac{(x/2)^4}{2!(1+n)(2+n)} - \dots \right\},$$

$$I_n(x) = \frac{x^n}{2^n \Gamma(n+1)} \left\{ 1 + \frac{(x/2)^2}{1!(1+n)} + \frac{(x/2)^4}{2!(1+n)(2+n)} + \dots \right\}.$$

For large real values of x , $I_n(x)$ has the asymptotic expansion,

$$I_n(x) = \frac{e^x}{(2\pi n)^{1/2}} \left\{ 1 + \frac{1^2 - 4n^2}{1! 8x} + \frac{(1^2 - 4n^2)(3^2 - 4n^2)}{2! (8x)^2} + \dots \right\}.$$

It possesses the recurrence formula,

$$I_{n-1}(x) - I_{n+1}(x) = \frac{2n}{x} I_n(x).$$

Note.—We are indebted to the Trustees of the Dixon Fund of the University of London for a grant in aid of the computations contained in this paper and in the two preceding papers (Proc. Roy. Soc. ci. pp. 493–528) (1922); Phil. Mag. xlv. pp. 846–849 (1923)).

* Communicated by the Authors.

† For an extensive bibliography of the subject, see G. N. Watson's 'Theory of Bessel Functions' (1923).

Tables of Bessel Functions.

TABLE I.

x .	$I_0(x)$.	$I_1(x)$.	$I_2(x)$.	$I_3(x)$.	$I_4(x)$.	$I_5(x)$.	$I_6(x)$.
16	893440	865053	753307	608728	534331	401459	283630
17	235494	228461	208619	179376	145312	110895	800203
18	621838	601316	554688	481060	394347	305785	224460
19	164461	160075	147611	128099	106877	839064	626673
20	435583	424553	393127	343926	299351	230188	174292
21	115514	112729	104777	927709	782714	629333	482042
22	300695	290639	279451	248828	211392	171889	133458
23	815139	797224	743822	667516	571676	468661	367918
24	216863	212294	199168	179103	154397	127636	101214
25	577452	565783	532191	480634	416834	347243	277939
26	154066	151075	142445	129180	112641	943039	762948
27	410420	402745	380592	340365	303617	256408	208656
28	109534	107561	101852	930113	819211	696042	570616
29	292519	287434	272987	249820	221013	188852	155889
30	781674	768535	730434	671138	596213	512141	425494
31	208995	205598	195732	180342	160827	138839	110041
32	559092	550288	524700	484699	439823	376242	316250
33	149637	147354	140707	130298	117018	101931	861273
34	400886	394760	377465	350340	315642	276070	234438
35	107339	105794	101294	942181	851412	747574	637832
36	287664	283643	271910	253432	229671	202396	173447
37	771245	760745	730124	681225	619652	547814	471467

TABLE II.

x .	$\sqrt{2\pi x}$.	e^x .	$\frac{e^x}{\sqrt{2\pi x}}$
21	11.4868	1318820000	1148110000
22	11.7571	358491	304914
23	12.0214	974480	810624
24	12.2799	264891	215711
25	12.5331	720049	574516
26	12.7666	195730	153313
27	13.0248	532048	408488
28	13.2638	144626	109038
29	13.4986	393133	291240
30	13.7294	106865	778366
31	13.9563	290488	208141
32	14.1796	789630	556876
33	14.3995	214644	149063
34	14.6160	583462	399193
35	14.8294	158601	106951
36	15.0398	431123	286656
37	15.2472	117191	768608
38	15.4519	318559	206162
39	15.6539	865934	553175
40	15.8533	235385	148477

TABLE III.

x .	J_2^x / I_2^x .
1	.846721
2	.512121
3	.216506
4	.056694
5	.002660
6	-.005192
7	-.002430
8	-.000345
9	.000167
10	.000112
11	.000023
12	-.000005
13	-.000005
14	-.000001
15	.000000

TABLE IV.

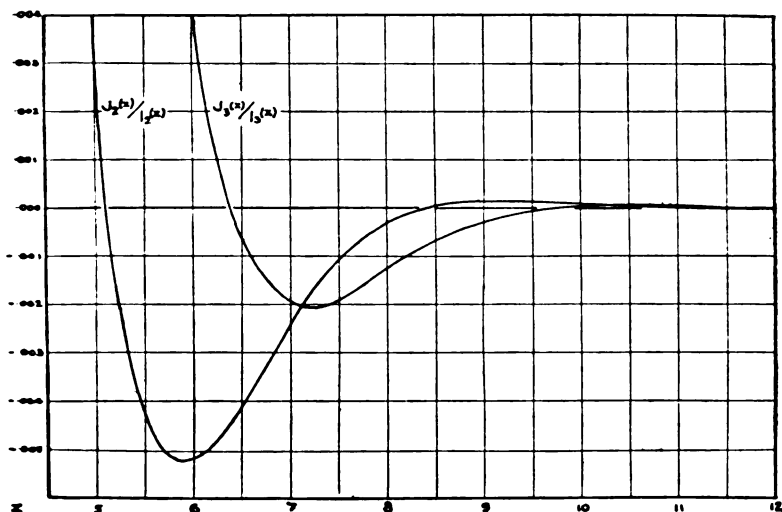
x .	$J_3(x) / I_3(x)$.
1	.882273
2	.606018
3	.322046
4	.128907
5	.035312
6	.003808
7	-.001968
8	-.001233
9	-.000280
10	.000033
11	.000048
12	.000015
13	.000000
14	-.000002
15	-.000001

The Table I. and the subsidiary Table II. are in continuation of tables given in a previous paper *. The values of $I_n(x)$ have been calculated directly from the asymptotic expansion, and the recurrence formula was used as a check. The tables are correct to five significant figures.

Tables III. and IV. give the values of the quotients

$$J_2(x)/I_2(x), \quad J_3(x)/I_3(x).$$

Fig. 1.



These quotients are of importance in certain problems in acoustics †. Graphs of these functions between the limits $x=5$ and $x=12$ are included. They have been calculated from the values of $I_n(x)$ previously given, and the values of $J_n(x)$ given in Jahnke and Emde's 'Funktionentafeln' (Leipzig and Berlin, 1909).

* Cf. Phil. Mag. xlv. pp. 846-849 (1923).

† See Proc. Roy. Soc. ci. pp. 493-508 (1922).

VI. *The Application of Oscillating Valve Circuits to the Precise Measurement of Certain Physical Quantities.* By J. E. P. WAGSTAFF, M.A., *Lecturer in Physics at the University of Leeds* *.

IT has been shown by Whiddington† and others that the valve circuit can be employed very effectively to solve problems of pure Physics. In the present paper the scope of its usefulness has been extended by applying it to several quite diverse problems. Moreover, the applicability of the simple formula for the frequency of a valve circuit, $n = \frac{1}{2\pi\sqrt{LC}}$, has been fully investigated both for audible and high-frequency oscillations, and its limitations discussed.

Description of Apparatus.

The apparatus used is shown in fig. 1. V_1 and V_2 are oscillating valve circuits, the coils H, K, M, and N of which are so chosen as to produce oscillations of about a million frequency. Each pair of coils is mounted on a substantial wooden frame, and the anode and grid coils are insulated from one another by a layer of paraffin-wax paper. The variable vane condensers E and L serve to adjust the frequencies of the two circuits, and fine adjustments are effected by means of a small parallel plate condenser F in parallel with E. This is worked by means of a long ebonite arm G which projects from the box containing the condensers. The filaments of the two lamps are in parallel and are heated by means of a four-volt battery B (the negative pole of which is earthed) of as large a charging capacity as possible. It is also very important that the accumulators supplying the current to the filaments should be in excellent condition, as the success of this type of experiment depends largely on the constancy of the filament current. D is a battery of accumulators of E.M.F.=50 volts and supplies the high tension to both circuits, as shown. P is a Brown pattern loud-speaking telephone, mounted on a wooden platform above the apparatus, which emits quite a clear, constant, audible note when the circuits are working and in adjustment. No amplifier is used, as it seems best to avoid, wherever possible, all complications of the apparatus. All the wiring is of stout copper (enamel covered), and the joints

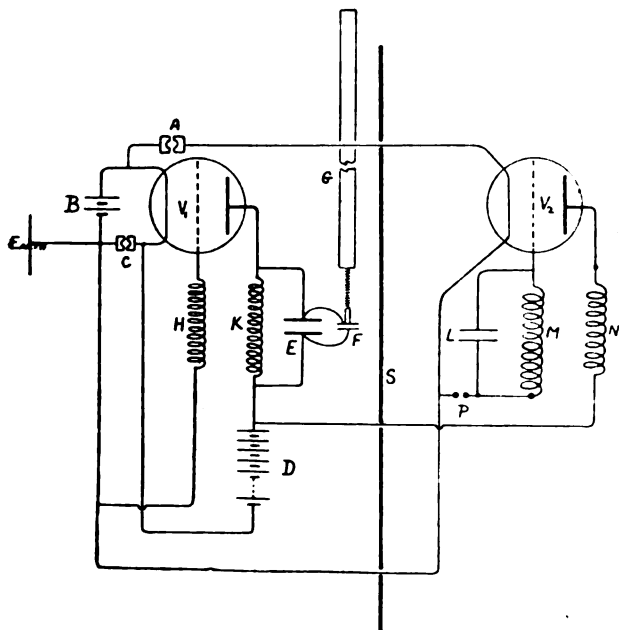
* Communicated by Prof. R. Whiddington.

† Whiddington, *Phil. Mag.* Nov. 1920.

are made as nearly perfect as possible. The apparatus is contained in four wooden cases lined with tinfoil, and covered on the outside with substantial tin sheeting, the inner and outer coatings of each box being in electrical contact and earthed. The whole is mounted on a solid stone slab. All wires passing from one box to another are protected in ebonite tubing. The two valves for maintaining the oscillations are fitted to the top of one of the boxes.

Experience has taught me that it is only when conditions are very quiet that the apparatus works satisfactorily. A

Fig. 1.



footfall overhead, the slamming of a door in a distant part of the building, is sufficient to produce a small change (usually one or two beats per sec.) in the frequency of oscillation. Consequently it has been necessary to do most of the work described in this paper between the hours of midnight and 3 A.M., when conditions are as nearly perfect as possible. When proper conditions are obtained the beats are remarkably steady; there is always a tendency for a slight variation, and this I attribute, as a result of a long and careful investigation, to variations in

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the battery B. The kind of steadiness obtained is given in the following table, where the time of 50 beats is tabulated against the interval between observations:—

TABLE I.

Interval between observations.	Time for 50 beats.
0	18.5 sec.
1 min. later	18.0 "
2 "	17.5 "
3 "	17.2 "
5 "	16.6 "
6 "	16.5 "
7 "	16.0 "
8 "	16.0 "
9 "	16.0 "

In order to provide an unvarying standard of pitch to which the note can be adjusted, another valve circuit V is set up with capacities and inductances so large as to produce an audible note in the telephone placed in the anode circuit. A separate filament battery and high-tension battery are used for this circuit. The capacity consists of a standard condenser box having a range of capacities from .001 m.f. to 1 m.f.

Standardization of the Oscillating Circuits.

When the circuits had been constructed as indicated in the last paragraph, and beats of steady frequency could be heard when the three circuits were oscillating, the various parts were accurately calibrated.

Calibration of the Oscillating Circuit of Audible Frequency.

For this experiment a set of standard tuning-forks was employed. The note emitted by the audible circuit was altered by accurately adjusting the capacity in the standard condenser, keeping everything else in the circuit constant, until resonance was obtained between the circuit and a given fork (*i.e.*, until no beats could be detected). With the higher notes ($n=1024$, $n=1536$, etc.) the experiment was slightly modified by adjusting the capacity in the box until the audible note was an octave of the fork. In the neighbourhood of the correct capacity beats became quite audible. It was rather difficult to decide at times with the ear, owing to the difference in quality of the two notes, which octave of the fork was being emitted. This was easily settled, however, by counting the number of beats

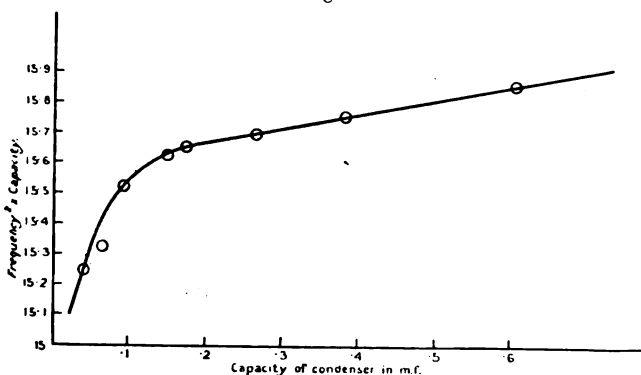
produced per second between the fork and the circuit, corresponding to a small change in the capacity of the latter. In the table below is shown the capacity in the box for various frequencies of note emitted. The numbers have been checked from time to time and have shown no material variation over a period of eight months.

TABLE II.

Frequency of note.	Capacity in box. m.f.	$n^2C \times 10^{-4}$.	$\cdot 26C - \frac{0.022}{C}$.	$n^2(C + \bar{c}) \times 10^{-4}$.
512	·605	15·86	+·12	15·92
643	·381	15·76	+·04	15·82
768	·266	15·70	−·0135	15·80
955	·172	15·66	−·04	15·85
1024	·149	15·63	−·109	15·81
1286	·094	15·53	−·21	15·85
1536	·065	15·33	−·3216	15·76
1929	·041	15·25	−·526	15·92

It is seen that n^2C is not constant, but tends to decrease as the frequency increases. In fig. 2 columns 1 and 3 have been plotted.

Fig. 2.



The relationship between n^2C and C is represented by the equation

$$n^2C = 10^4 \left(15.74 + 0.26C - \frac{0.022}{C} \right).$$

This is best seen by plotting n^2C against $\left(\cdot 26C - \frac{0.022}{C} \right) 10^4$.

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The corresponding values of the two variables for different values of C are given in columns 3 and 4 of Table II. A straight-line relationship, which is of course purely empirical, is indicated between the variables. Incidentally the term 15.74×10^4 , which is independent of C , can be used to find the self-induction of the anode coil. It is the constant in the expression, and can be identified with $\frac{1}{4\pi^2 L}$. It has been found possible to interpret the results differently. The quantity C , up to now, only takes into account the capacity of the oscillating circuit introduced by the condenser, and this is calibrated for static fields. If a capacity $\bar{c} = .0018$ m.f. be added to C , $n^2(C + \bar{c})$ is seen to be constant to an accuracy of 1 per cent. over the range of frequencies used. Hence for an audible circuit of constant self-induction, $n^2 C$ is constant in accordance with the law $n = \frac{1}{2\pi \sqrt{LC}}$, provided a sufficiently broad interpretation of C is taken.

Standardization of the High-frequency Circuit.

Having justified the assumption that the frequency in the case of audible circuits is represented within 1 per cent. by a formula of the form $n^2(C + c) = \text{constant}$, I directed my attention to the corresponding problem in the case of the valve circuit of high-frequency oscillations. The condenser used in this circuit was of the variable vane type, and this was first calibrated with a ballistic galvanometer so that the absolute capacity was known corresponding to any position of the vanes. The procedure was that usually adopted in this type of problem, the condenser being charged up by connecting its terminals to the pole of a battery of E.M.F. = 200 volts, and subsequently discharged through a suitable galvanometer.

The results were standardized by discharging through the galvanometer condensers of known capacity. The relationship between the capacity and the scale-reading was found to be linear and of the form

$$C_{\text{m.f.}} = 10^{-5}(87.04 - .3758x),$$

where x is the scale-reading.

At this stage, keeping everything else constant (*e. g.* battery potentials, inductances, etc.), the wave-lengths of the oscillations generated in the circuit were measured by a standard wave-meter for various values of the capacity, and the results afterwards confirmed with a Fleming cymometer. The results are tabulated here.

TABLE III.

Scale-reading.	Capacity C. m.f.	Wave-length λ . cm.	Frequency = $\frac{c}{\lambda}$.	Frequency ² .	Frequency ² × C.	Frequency ² (C + c).
174	21.67×10^{-5}	2.130×10^5	1.492×10^8	2.226×10^{16}	48.25×10^8	107.98×10^8
140	34.44×10^{-5}	2.255×10^5	1.330×10^8	1.769×10^{16}	60.94×10^8	108.4×10^8
120	41.95×10^{-5}	2.414×10^5	1.243×10^8	1.545×10^{16}	64.79×10^8	106.24×10^8
100	49.46×10^{-5}	2.555×10^5	1.174×10^8	1.378×10^{16}	68.17×10^8	105.15×10^8
80	56.98×10^{-5}	2.681×10^5	1.119×10^8	1.251×10^{16}	71.31×10^8	105.15×10^8
60	64.49×10^{-5}	2.801×10^5	1.071×10^8	1.148×10^{16}	73.98×10^8	104.87×10^8
40	72.01×10^{-5}	2.877×10^5	1.043×10^8	1.087×10^{16}	78.3×10^8	107.40×10^8
20	79.524×10^{-5}	2.977×10^5	1.008×10^8	1.015×10^{16}	80.74×10^8	107.98×10^8

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It will be noticed that n^2C is here not even approximately constant, so that either $n = \frac{1}{2\pi\sqrt{LC}}$ can no longer be applied or a much broader interpretation of C is necessary. n^2C can be shown to be related to C by an empirical equation of the form

$$n^2C = 61.411 \times 10^5 + \left(.3133 \times 10^{10} C - \frac{432.5}{C} \right).$$

The similarity in the relationships between frequency and capacity for low-frequency and high-frequency circuits is in this way strikingly demonstrated. In each case a simple equation of the form

$$n^2C = A + BC + \frac{D}{C}$$

suffices to represent the relationship. An attempt was again made to interpret the results on the lines indicated in the last section. Assuming, as the results up to now indicate, that the relationship between frequency and capacity for high-frequency oscillations does not differ fundamentally from that deduced for low-frequency oscillations, it is justifiable to write

$$n^2(C + \bar{c}) = \text{constant}.$$

Taking the first and last values of n and C in the above table, the equation becomes

$$48.25 \times 10^5 + 2.226 \times 10^{10} \bar{c} = 80.74 \times 10^5 + 1.015 \times 10^{10} \bar{c}.$$

$$\bar{c} = 26.83 \times 10^{-5} \text{ m.f.}$$

This is the additional capacity to be added to C .

If this additional capacity $\bar{c}$ remains approximately constant for the range of wave-lengths used,

$$n^2(C + 26.83 \times 10^{-5}) = \text{constant}.$$

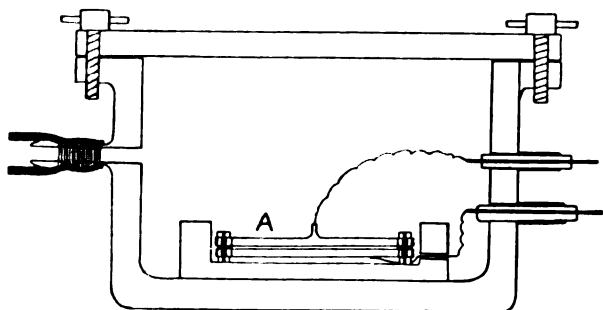
In the last column of the above table is calculated $n^2(C + 26.83 \times 10^{-5})$ for the values of C given in column 2.

The values are constant to within 3 per cent., and this variation can probably be further reduced by choosing a more judicious value for $\bar{c}$. Thus it follows that for low- and high-frequency circuits, $n^2(C + c)$ is reasonably constant, where c is a suitably chosen capacity for each circuit used.

*Determination of the Dielectric Constant of Air and
its Variation with Pressure.*

The first series of experiments undertaken with the above apparatus was the determination of the dielectric constant of air and its variation with pressure. The condenser (fig. 3) used in this investigation consisting of two steel plates $\frac{1}{4}$ in. $\times$ 3 in. $\times$ $\frac{1}{4}$ in., separated by circular plugs of ebonite 1 mm. thick, was placed in parallel with the variable vane condenser E. The plates were clamped together by means of screw pins and small nuts as shown. The pins were insulated from the condenser plates by passing them through ebonite plugs inlaid in the plates, concentric with those separating the plates and very slightly smaller than the latter in diameter, and the nuts were screwed down on these.

Fig. 3.



The condenser rested in an ebonite cradle to insulate it from the wall of the pressure chamber, which was earthed. The pressure chamber consisted of a very strong brass casting, with $\frac{3}{4}$ in. walls, connected to the exhaust pump through the side tube by pressure tubing. Thick brass wires, fitted in fibre plugs and passing through the side of the vessel as shown, served as leads to the condenser. To ensure that any slight contraction of the chamber produced no strain on the condenser plates, the leads were joined to the plates by two small coils of very fine, insulated, copper wire.

Precautions of the kind just described are essential in experiments with valve circuits, otherwise the effects to be measured are completely masked by spurious effects arising from such causes as change in the size or shape of the pressure chamber, or in the disposition of the condenser plates inside the chamber.

The top of the casting was secured to the body by

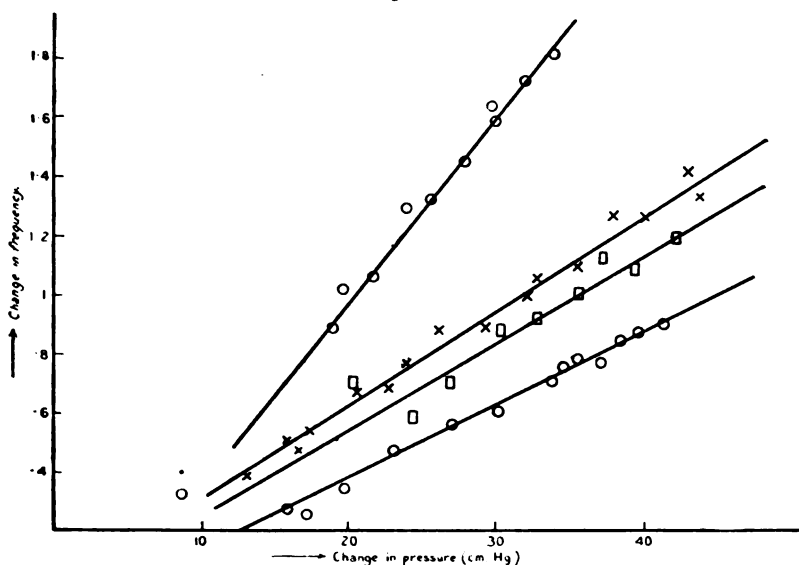
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thumb-screws, and a piece of indiarubber placed between the two was found very useful in rendering the apparatus air-tight. An ordinary mercury manometer served to register the pressure inside the chamber.

Method of procedure.

The valve circuits V , V_1 , and V_2 were made to oscillate, and the capacities were adjusted until slow beats at the rate of about 2 per second could be heard in the telephones. The vessel was now partially exhausted, and when conditions were steady again the time for 50 or 100 beats was

Fig. 4.



measured with a stop-watch. The pressure was immediately released, and the time of 100 beats again measured. Various initial pressures varying from 10 to 40 cm. were used, and the series was repeated for various frequencies of oscillation. In this way the change of frequency of the circuit V_1 was measured for a given change of pressure inside the chamber. Fig. 4 shows the "change in pressure" plotted against "corresponding change in frequency" for all the frequencies used, and it is evident that the change in frequency is a linear function of the change in pressure.

In order to calculate the dielectric constant of air from the observations the capacity of the condenser had still to

be determined. This was done with a heterodyne beat method, by finding the change in the frequency of the audible circuit, when the parallel plate condenser and its earthed case were connected in parallel with the standard condenser. The determination was repeated for several frequencies of the circuit, and very good agreement was obtained.

That the method is capable of giving reliable results was confirmed by substituting for the condenser A a condenser of known and calculable capacity. Excellent agreement was obtained with the calculated value and with the value determined by electrostatic methods.

We are now in a position to calculate the dielectric constant of air.

The frequency of an oscillating circuit is given by the equation

$$n = \frac{1}{2\pi\sqrt{LC}},$$

where C is the *total* capacity of the circuit, and L is the coefficient of self-induction of the anode circuit.

Corresponding to a change in capacity dC , the frequency is

$$n - dn = \frac{1}{2\pi\sqrt{L(C + dC)}},$$

therefore
$$\left(\frac{n}{n - dn}\right)^2 = \frac{C + dC}{C},$$

i. e.
$$\frac{2dn}{n} = \frac{dC}{C}.$$

If c_1 is the capacity of the parallel plate condenser A (fig. 3), and the change in capacity dC is due to the withdrawal or admission of air into the chamber containing A,

$$dC = c_1(K - 1)\frac{p_1}{\Pi},$$

where p_1 is the change of pressure in the chamber, and Π is the atmospheric pressure.

Therefore
$$K - 1 = \frac{2\Pi}{n} \cdot \frac{C}{c_1} \cdot \frac{dn}{p_1}.$$

For a particular value of n , $\frac{dn}{p_1}$ is given by the slope of the appropriate line in fig. 4.

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The values of $K-1$ for the values of C employed are shown in the following table :—

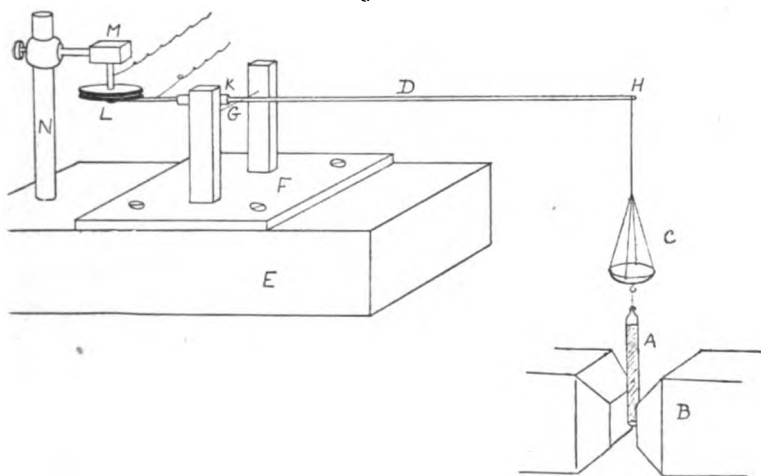
TABLE IV.

c_1 (mean value of 27 observations) = 5.50×10^{-5} m.f.

Scale-reading.	Capacity of vane condenser.	Total capacity C .	Frequency of oscillations.	$K-1$.
40	72.01×10^{-5} m.f.	104.34×10^{-5} m.f.	1.015×10^5	.0006817
80	56.98×10^{-5} m.f.	89.31×10^{-5} m.f.	1.083×10^5	.0006612
120	41.95×10^{-5} m.f.	74.28×10^{-5} m.f.	1.196×10^5	.0005976
174	21.67×10^{-5} m.f.	54.00×10^{-5} m.f.	1.415×10^5	.0006639

The values obtained for $K-1$ are in good agreement with those obtained by other investigators. These results therefore confirm the hypotheses made earlier in the paper.

Fig. 5.



Application of the Oscillating Valve Circuit to the Determination of Magnetic Susceptibilities for Steady Fields.

The arrangements used for applying this method to the measurement of magnetic susceptibility in steady fields are shown in fig. 5. The upper plate of an air condenser L

is clamped to a vertical upright N fixed rigidly to a steel base E which is earthed. An ebonite plug M serves to insulate the plate. The lower plate is fastened to a long brass rod D (being insulated from it by the ebonite plug K), and is suspended between two stout vertical uprights F by means of a thin horizontal steel wire G about 3 in. long. This wire, which is soldered to the brass rod D, is drawn through the two vertical uprights under tension and fastened securely to them. Thus the lower plate of the condenser and the rod can move in a vertical plane, and the motion is controlled by the torsion of the wire G. This apparatus is contained in an earthed case, with the arm D projecting. The specimen A to be examined is suspended from H so as to lie symmetrically between the poles of an electromagnet B. For purposes of calibration it has been found convenient to include a scale-pan C in the suspended system.

Before commencing the experiment, by means of sliding weights fixed to the arm D, the lower plate of the condenser is adjusted so as to lie horizontal when free, and the upper plate is clamped at a vertical distance of 1 mm. above it. The arrangement replaces the condensers E and F in fig. 1. The current to the electromagnet is obtained from a large battery of accumulators, and the circuit includes an ammeter, rheostat, and plug. A commutator is also arranged in the circuit for reversing the current through the coils of the electromagnet.

Theory.

The above apparatus is essentially a delicate torsion-balance, which is capable of measuring small changes in the tension applied at H. In the experiments to be described, it has been found comparatively simple by this method to measure $\frac{1}{4}$ dyne, but $\frac{1}{100}$ part of this amount can also be estimated. It can be proved that if a specimen of cross-section A and susceptibility μ is suspended in a horizontal magnetic field of varying intensity, there is a pull P vertically downwards on the specimen, where

$$P = \frac{\mu A}{2} (H_0^2 - H_1^2) *,$$

H_0 and H_1 being the strengths of the magnetic field at the two ends. For a long rod $H_1 = 0$, and the expression for P reduces to

$$P = \frac{\mu H_0^2 A}{2}.$$

* Maxwell, 'Electricity and Magnetism,' 3rd ed. vol. ii. p. 74.

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Thus by switching on the current through the electromagnet, the pull applied to H is altered by a definite amount. This produces a small change in the distance between the two plates of the condenser L, and if the circuit V_1 is oscillating, a slight change occurs in the frequency of oscillation. This can be measured by means of the auxiliary circuits V_2 and V.

Method of experiment.

When the torsion-balance was fitted up as explained above, and the specimen suspended symmetrically between the pole-pieces of the electromagnet, the valve circuits V_1 , V_2 , and V were set oscillating and the capacities adjusted until slow beats could be heard. The time for 50 beats was measured with a stop-watch, the current through the electromagnet switched on, and the time for 50 beats again measured, the current registered by the ammeter being carefully noted. When the field was switched off, a third measurement of the frequency of the beats was made and any slight change due to drift eliminated.

The results obtained for a rod of bismuth are given below :—

Diameter of section of rod = .643 cm.

Current in electromagnet = 5 amp.

Capacity in audible circuit = .157 m.f.

Change in frequency of V_1 when current through the electromagnet is switched on = 5.486 oscil./sec.

The above change in frequency is the mean value of 29 observations, which show extreme variations of ± 0.1 about the mean. In order to interpret these readings, definite loads were added to the scale-pan C, and the change in frequency of the circuit V_1 determined. It was also noticeable that whereas the addition of weights made the beats faster, switching on the field made them slower. This corresponds to a negative coefficient of susceptibility in the case of bismuth.

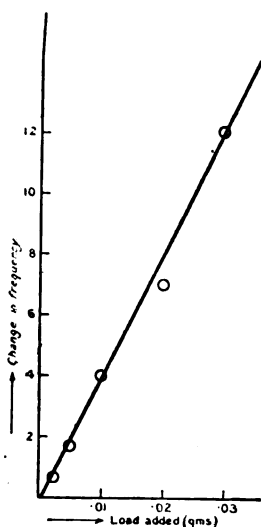
TABLE V.

Mass added to scale-pan.	Change in frequency of V_1 .
.002 gm.	.663
.005 „	1.715
.01 „	4
.02 „	7
.03 „	12

In fig. 6 the values recorded in the above table are plotted, and it is obvious that for small loads a linear relationship exists between the change in frequency of V_1 and the load added to the scale-pan. From the curve, the load corresponding to a change in frequency of 5.486 is found to be .0137 gm.

The experiment with bismuth was repeated, with the plates of the condenser L so close together that quite an appreciable change of note occurred when the current through the electromagnet was switched on. In this case

Fig. 6.



the change in frequency of V_1 was estimated by altering the capacity of the audible circuit V until resonance was again obtained, and calculating from the constants of that circuit the change in frequency corresponding to the given change in capacity. The results are given below :—

Current through electromagnet = 5 amp.

Mean change in frequency of V_1 when current through electromagnet is switched on = 72, with an extreme variation for 6 observations of ± 4 about the mean.

The readings were again standardized by adding known weights to the scale-pan, and finding the corresponding change in frequency of the note emitted by the circuit.

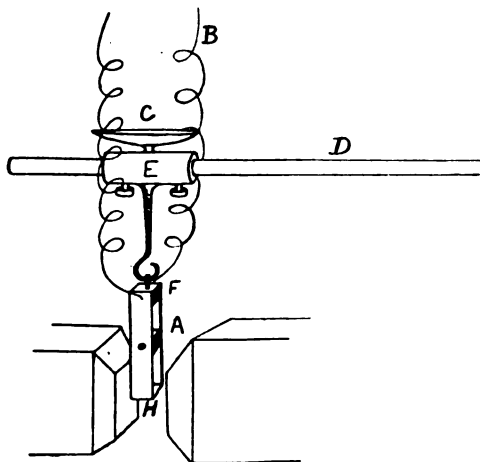
The alteration in load corresponding to a change in frequency of 72 was found to be .0128 gm. wt.

Determination of the Strength of the Magnetic Field between the Poles of the Electromagnet.

Before the magnetic susceptibility could be calculated, it was necessary to find the value of H_0 —the magnetic field between the pole-pieces. This was done by two independent methods, and the results were compared.

In the first method a small test coil was wound on a flat plate of ebonite $\frac{1}{2}$ cm. long, .6835 cm. wide, and .162 cm. thick with enamel-covered wire of the finest gauge. This coil was arranged in series with a ballistic galvanometer and the secondary of a standardizing coil, and placed midway between the poles of the electromagnet so that the turns of the coil cut the lines of the field at right angles. The throw obtained when the current through the electromagnet was reversed was compared with that obtained when a suitable current through the primary of the standardizing coil was similarly reversed. As a result of several observations, H_0 was found to be 2414 gauss.

Fig. 7.



In order to confirm the above value of H_0 , a second determination was made by finding the force on a current circuit placed in the position H between the pole-pieces of the electromagnet. The arrangement used is shown in fig. 7. The frame A consists of two parallel vertical copper strips 3 in. long, $\frac{1}{2}$ in. wide, and $\frac{1}{32}$ in. thick, to the bottom of which is soldered a horizontal cross-piece of copper, of rectangular section and of the same area approximately as the

bismuth rod. Small pieces of ebonite screwed to the strip at F and F' serve to keep them quite parallel. This frame is hooked to a sliding-piece E, which can be fixed anywhere along the arm D, and which supports the scale-pan C. The current to A is conveyed through two spiral coils of extremely fine copper wire B. The circuit containing A includes a reversing commutator, a reliable milliammeter, resistance-box, key, and a 2-volt battery.

Method of experiment.

The suspended frame was first of all adjusted so that the current through the horizontal cross-piece flowed perpendicular to the lines of the magnetic field. The circuits were made to oscillate as before, the capacity in the audible circuit being adjusted until extremely slow beats (one in two seconds) could be heard between the circuits. A current was sent through the frame and the capacity altered until beats of the same frequency were again audible. Then, from the known constants of the audible circuit, the change in frequency of V_1 was immediately determined :

Current through cross-piece = .038 amp.

Length of conductor = .734 cm.

Mean change in frequency of V_1 on switching on current through electromagnet = 24.46.

The readings were again calibrated by adding known weights to the pan and observing the corresponding change of frequency, and it was found that a change of frequency of 24.46 corresponded to an additional pull of .00695 gm. wt. Now, if a conductor of length l cm., carrying a current i e.m.u., is situated in a field of intensity H_0 , there is a mechanical force on the conductor perpendicular to the plane of i and H_0 and of magnitude P given by

$$P = i l H_0.$$

It is obvious that the vertical sides of the frame give no contribution to the resultant force downwards.

Hence, since $i = \frac{.038}{10}$ e.m.u.,

$l = .734$ cm.,

$P = .00695 \times 981$ dynes,

and $H_0 = 2444$ gauss,

which agrees with the previous determination to an accuracy of about 1 per cent.

Phil. Mag. Ser. 6. Vol. 47. No. 277. Jan. 1924. G

82 Mr. Wagstaff : *Application of Oscillating Valve Circuits*

The susceptibility of bismuth can now be calculated from the formula $\mu = \frac{2P}{AH_0}$:

The first series of experiments gives $\mu = -13.86 \times 10^{-6}$,

The second " " " $\mu = -12.94 \times 10^{-6}$,

for which the mean value is -13.4×10^{-6} , and this is in very close agreement with the best values previously obtained.

The magnetic liquid Nickel Carbonyl was next investigated by this method. Although the susceptibility of this liquid is of a much lower order than that of bismuth, the method has given consistent results for μ . The liquid was contained in a tube and suspended from the arm D as before. The operations were carried out in exactly the same way as described in the previous experiment. Owing to the small susceptibility of the liquid, changes of frequency had to be estimated by the beat method throughout. The results of the two series of observations taken are given below :—

SERIES I.

Mean diameter of tube = .6781 mm.

Current through electromagnet = 5 amp.

Mean change of frequency = -1.400 , which corresponds to a change in tension of $-.00037$ gm. wt. The negative sign indicates that the liquid is diamagnetic.

SERIES II.

Mean diameter of tube = .9467 mm.

Current through electromagnet = 5 amp.

Mean change of frequency = $-.1979$, which corresponds to a change in pull on the arm D of $-.00063$ gm. wt.

From Series I.

the susceptibility of nickel carbonyl = $-.34 \times 10^{-6}$,

and from Series II.

the susceptibility of nickel carbonyl = $-.30 \times 10^{-6}$.

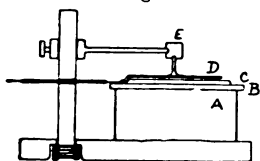
The method is thus capable of measuring low order susceptibilities.

In the above, calibration experiments were carried out for each set of observations taken. This is not at all necessary, generally, but for the preliminary set of experiments it was thought desirable to perform them under widely varying conditions so as to test the kind of accuracy that was to be expected.

Experiments to investigate the Effect of Electrostatic Charge on the Surface Tension of a Mercury-Air Surface.

Recently I became interested in the question of the effect on its surface tension of charging up a mercury surface, and devised an experiment to demonstrate its existence or otherwise. The oscillating valve circuits of the previous sections were again utilized in a manner shown in fig. 8.

Fig. 8.



A large drop of mercury (C) was placed on a plate of perfectly clean glass B, which rested on a steel slab A, fixed to a strong stand. Electrical contact with the drop was maintained by means of a thin platinum wire, fused into a glass tube filled with mercury, which just pierced the surface of the drop. A metal plate D was fixed above the upper surface of the drop by clamping it to the same stand. An ebonite plug E served to insulate D from the stand. The distance between C and D was adjusted to be about $\frac{1}{2}$ mm. by a fine screw fixed to D, unfortunately omitted from the drawing. C and D being only $\frac{1}{2}$ mm. apart, it was very difficult at times to keep them separate; the slightest vibration brought the mercury into contact with the plate, and the various adjustments had then to be repeated. In one series, to prevent this, a very thin glass cover-slip was made to rest on the surface of the mercury, and this was found to overcome the difficulty completely. The above arrangement constituted a parallel plate condenser, of which D formed one plate and the mercury drop the other, and was substituted for E and F (fig. 1). The potential of the battery D was reduced as much as possible, and the earthed wire at C was removed.

Theory.

Since the condenser formed by D and the mercury constitutes most of the capacity in the circuit V_1 , any change in the distance CD will profoundly modify the frequency of oscillation of that circuit. This distance will be changed if, due to any cause, the thickness of the drop is made to change, and any alteration in the surface tension of the mercury will effect this. It has been estimated that a change in the thickness of the drop of 10^{-6} can be detected.

Method of experiment.

The circuits V_1 , V_2 , and V were made to oscillate, and the capacities adjusted until slow beats (2 or 3 per second) could be heard. The mercury drop was earthed and the frequency of the beats counted. The earth was now removed, and the bubble placed in electrical contact with the positive pole of a battery of E.M.F. = 200 volts, the negative pole of which was earthed, and the frequency of the beats again measured.

No change whatever could be detected.

Hence it must be concluded that no variation in the surface tension of the mercury resulted when the drop was charged to a potential of 200 volts.

In conclusion, I wish to express my thanks to Professor R. Whiddington for his interest in the work and for his helpful suggestions, and to the Grants Committee of the Royal Society who helped to defray the cost of the apparatus.

University of Leeds,
August 8th, 1923.

VII. *The Characteristic Vibration Frequency of an Element.*

By J. E. P. WAGSTAFF, M.A., Fellow of St. John's College, Cambridge, Lecturer in Physics at the University of Leeds.*

FROM considerations of the distribution of atoms in a substance and the forces acting on them when they are displaced from their positions of equilibrium, Einstein † has shown that the characteristic frequency ν of the body can be determined in terms of the compressibility κ , the atomic volume V , and the atomic weight M by means of the formula

$$\nu = \beta \frac{V^{1/6}}{\kappa^{1/2} M^{1/2}}, \quad \dots \dots \dots (I.)$$

where $\beta = 2.54 \times 10^7$.

Speculations on certain results I have been obtaining have led me to investigate the amount and nature of the variation that occurs in the quantity β (theoretically a constant) in the above formula as one passes from element to element, and the results seem of sufficient interest to

* Communicated by the Author.

† Einstein, *Annalen der Physik*, **xxxiv.** p. 170 (1911).

publish. Incidentally, an instructive method of deriving (I.) has been evolved and is included in the paper.

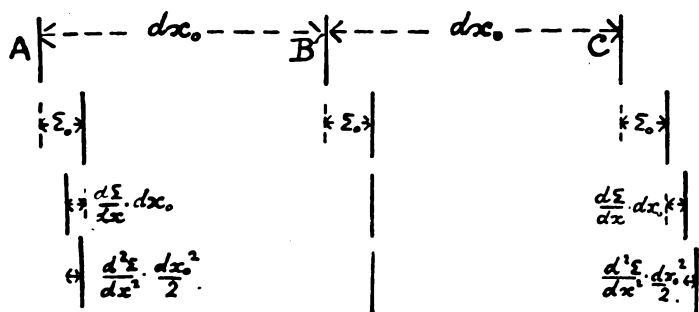
Suppose the substance contains atomic vibrators of frequency ν , then according to the simple theory of harmonic motion,

$$\frac{1}{\nu} = 2\pi \sqrt{\frac{m}{f}},$$

where m is the atomic mass, and f is the restoring force corresponding to unit displacement from the equilibrium position, which is in all probability a position of symmetry with respect to adjacent layers. If one supposes the substance to be built up of small cubes of sides dx_0 , each cube containing one atom, dx_0 represents the initial distance between the successive layers.

Consider three such layers represented by the planes A, B, C (fig. 1), and suppose B is displaced an amount Σ_0 .

Fig. 1.



The displacement of C is

$$\Sigma_C = \Sigma_0 + \frac{d\Sigma}{dx} \cdot dx_0 + \frac{d^2\Sigma}{dx^2} \cdot \frac{dx_0^2}{2} + \dots$$

and the displacement of A is

$$\Sigma_A = \Sigma_0 - \frac{d\Sigma}{dx} \cdot dx_0 + \frac{d^2\Sigma}{dx^2} \cdot \frac{dx_0^2}{2} + \dots$$

The plane B is thus displaced from its position of symmetry with respect to the two adjacent planes by an amount $\frac{d^2\Sigma}{dx^2} \cdot \frac{dx_0^2}{2}$, and is therefore subjected to a force of magnitude $f \cdot \frac{d^2\Sigma}{dx^2} \cdot \frac{dx_0^2}{2}$ acting in the direction BC.

If the longitudinal stress at A is $\frac{P}{a}$, we can write

$$\frac{f}{2} \cdot \frac{d^2 \Sigma}{dx^2} \cdot dx_0^2 = \frac{dP}{dx} \cdot dx_0 \frac{dx_0^2}{a},$$

where a is the cross-section of the material.

$$\begin{aligned} \therefore P &= a \cdot \frac{f}{2 dx_0} \cdot \frac{d\Sigma}{dx}, \\ &= a \cdot \frac{2\pi^2 \nu^2 m}{dx_0} \cdot \frac{d\Sigma}{dx}. \end{aligned}$$

But in the case of a simple elongation of the material (lateral forces being applied so that no change in the lateral dimensions occurs in spite of the longitudinal tension), the longitudinal component of the stress is related to the strain by the equation

$$\frac{P}{a} = j \cdot \frac{d\Sigma}{dx},$$

$$\text{where } j = \frac{3(1-\sigma)}{\kappa(1+\sigma)},$$

κ being the compressibility and σ Poisson's ratio.

$$\begin{aligned} \therefore \frac{2\pi^2 m \nu^2}{dx_0} &= j = \frac{3(1-\sigma)}{\kappa(1+\sigma)}; \\ \therefore \nu &= \frac{1}{\pi} \left\{ \frac{3 dx_0 (1-\sigma)}{2 m \kappa (1+\sigma)} \right\}^{1/2}. \quad \dots \quad (II.) \end{aligned}$$

Suppose M is the atomic weight of the element, V the atomic volume, and ρ the density.

$$\text{Then } m = M \times 1.64 \times 10^{-24},$$

$$\text{and } \frac{m}{dx_0^3} = \rho = \frac{M}{V}.$$

Substituting for m and dx_0 in (II.),

$$\nu = 3.306 \times 10^7 \frac{V^{1/6}}{M^{1/2} \kappa^{1/2}} \left(\frac{1-\sigma}{1+\sigma} \right)^{1/2}, \quad \dots \quad (III.)$$

which reduces for $\sigma = \frac{1}{4}$, to

$$\nu = 2.56 \times 10^7 \frac{V^{1/6}}{M^{1/2} \kappa^{1/2}}$$

which is Einstein's formula.

In the following table the values of ν (derived from (III.)) for several elements are tabulated.

TABLE I.

Element.	σ .	Atomic Weight.	ν (From III.)	ν (From I.)	ν (Lindemann's melting-point method.)	ν (observed).
Copper	26	63.6	6.0×10^{12}	5.7×10^{12}	6.7×10^{12}	6.6×10^{12}
Lead	446	207	1.55 "	2.2 "	1.84 "	1.9 "
Aluminium ..	31	27.1	5.93 "	6.6 "	7.5 "	8.3 "
"	16		7.0 "	" "	" "	" "
Mercury.....	0	200	1.9 "	1.46 "	1.3 "	2.2 "
Iron	28	55.9	7.3 "	6.5 "	8.3 "	—
Bismuth	33	208	1.6 "	1.8 "	1.6 "	—
Cadmium	3	112	2.6 "	2.6 "	3.0 "	—
Gold	422	197	3.23 "	3.8 "	3.4 "	—
Nickel	31	58.7	8.27 "	6.6 "	8.2 "	—
Palladium	39	107	5.0 "	5.8 "	5.74 "	—
Platinum	39	195	5.0 "	4.6 "	4.36 "	—
Tin	33	119	2.6 "	2.8 "	2.24 "	—
Zinc	21	65.4	3.9 "	3.73 "	4.36 "	4.8×10^{12}

From the above table, it is seen that the values obtained for ν are in moderately good agreement with those given by Einstein and Lindemann.

Consider now the mean energy of an atomic vibrator of frequency ν and amplitude γ , whose motion is represented by an equation of the form $\Sigma = \gamma \sin 2\pi \nu t$. The energy associated with such a vibration $= 2m\pi^2\nu^2\gamma^2$, so that the energy associated with the vibration of atoms in a layer of thickness dx_0 and area a , containing N vibrators per unit volume $= 2m\pi^2\nu^2\gamma^2 Na dx_0$.

The work necessary to produce elastic oscillations of the same amplitude

$$= \frac{dP}{2} \cdot \gamma,$$

$$\text{where } dP = 2aj \frac{\gamma}{dx_0},$$

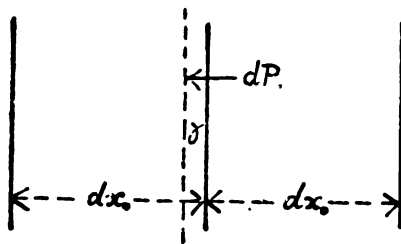
from the simple theory of stress and strain, j being the appropriate modulus of elasticity (fig. 2).

$$\begin{aligned}
 & \therefore \frac{\text{Energy associated with atomic vibrations of amplitude } \gamma}{\text{Work necessary to produce elastic oscillations of same amplitude}} \\
 &= \frac{\text{Energy associated with atomic vibrations of amplitude } \gamma}{\text{Energy associated with elastic vibrations of same amplitude}} \\
 &= \frac{2m\pi^2\nu^2 N d\epsilon_0^2}{j} \\
 &= \frac{2\rho\pi^2\nu^2\kappa(1+\sigma)V^{2/3} \times (1.64)^{2/3} \times 10^{-16}}{3(1-\sigma)} = 1,
 \end{aligned}$$

on substituting for $\frac{\nu^2\kappa V^{2/3}(1+\sigma)}{(1-\sigma)}$ from equation (III.), i. e.,

bodies for which the Einstein law holds are those whose atomic energy can be ascribed to the state of strain of the body.

Fig. 2.



As a further step we might suppose the quantity $\rho\kappa\nu^2 V^{2/3}$ is a measure of the ratio

$$\frac{\text{Energy associated with free atomic vibrations}}{\text{Energy associated with elastic vibrations}}$$

and that elements with values of $(\rho\kappa\nu^2 V^{2/3})^{1/2}$ large compared with 2.54×10^7 are those whose atomic energy is in excess of that accounted for as strain energy.

In Table II. values of $(\rho\kappa\nu^2 V^{2/3})^{1/2}$ have been tabulated for a large number of elements. The values of κ given are according to Richards*, while the values of V are due to Stefan Meyer†. The atomic frequencies have in general been calculated from Lindemann's melting-point formula, though, where known, observed values have been used instead.

In fig. 3, the quantity $(\rho\kappa\nu^2 V^{2/3})^{1/2}$ has been plotted against the atomic number of the element, and the observations joined

* Richards and Stull, *Zeitschrift für Phys. Chemie*, lxi. p. 183 (1908).

† *Elster and Geitel-Festschrift*, Braunschweig, p. 152 (1915).

TABLE II.

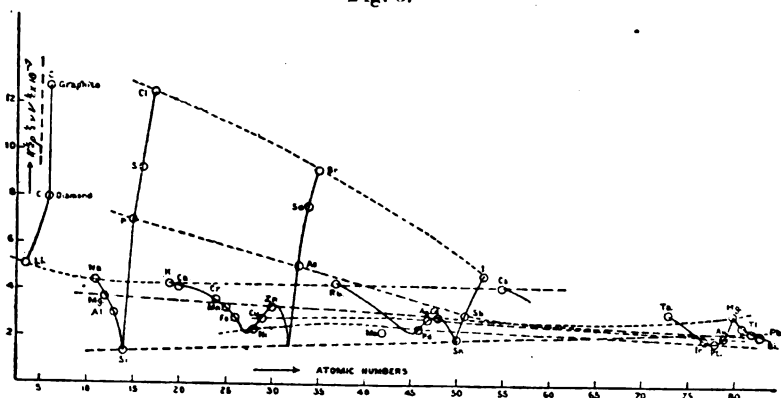
Element.	Atomic Volume.	$\nu \times 10^{-12}$.	κ .	ρ .	$\kappa^{\frac{1}{2}} \nu V^{\frac{1}{3}} \rho^{\frac{1}{3}}$.
Lithium.....	13.0	10.0	8.8×10^{-12}	0.534	5.097×10^7
Carbon Diamond	3.42	40.0	0.5	3.52	7.997
.. Graphite.	5.4	27.7	3.0	2.3	12.76
Sodium.....	23.7	3.96	15.4	0.98	4.42
Magnesium.....	13.4	7.2	2.7	1.74	3.706
Aluminium.....	10.0	7.5	1.3	2.6	3.03
Silicon.....	11.4	9.6	0.16	2.48	1.36
Phosphorus, Red.	14.4	6.3	9.0	2.34	7.03
Sulphur.....	15.5	7.3	12.5	2.07	9.26
Chlorine.....	25.0	3.68	95.0	1.42	12.5
Potassium.....	45.5	2.3	31.5	0.87	4.3
Calcium.....	25.9	4.9	5.4	1.53	4.17
Chromium.....	7.76	8.3	0.7	6.9	3.61
Manganese.....	7.43	7.5	0.67	7.37	3.25
Iron.....	7.1	8.3	0.4	7.85	2.83
Nickel.....	6.67	8.2	0.27	8.8	2.37
Copper.....	7.10	6.7	0.54	8.9	2.83
Zinc.....	9.5	4.8	1.5	7.13	3.32
Arsenic.....	13.3	4.36	4.3	5.64	5.13
Selenium.....	18.5	4.06	11.8	4.3	7.64
Bromine.....	25.1	2.45	51.8	3.19	9.22
Rubidium.....	56.2	1.45	40.0	1.52	4.33
Molybdenum.....	11.1	6.7	0.26	8.65	2.24
Palladium.....	9.3	5.46	0.38	11.4	2.39
Silver.....	10.3	4.36	0.84	10.5	2.82
Cadmium.....	13.6	3.0	1.9	8.6	2.895
Tin.....	16.2	2.24	1.7	7.3	2.0
Antimony.....	18.1	3.0	2.2	6.71	3.026
Iodine.....	25.7	2.0	13.0	4.95	4.73
Cæsium.....	70.6	0.95	61.0	1.89	4.216
Tantalum.....	10.93	4.75	0.54	16.6	3.156
Iridium.....	8.62	4.9	0.17	22.4	2.07
Platinum.....	9.1	4.36	0.21	21.3	1.926
Gold.....	10.2	3.4	0.47	19.24	2.218
Mercury.....	14.8	1.8	3.71	13.56	3.134
Thallium.....	17.2	1.84	2.6	11.83	2.634
Lead.....	18.2	1.84	2.2	11.4	2.429
Bismuth.....	21.2	1.63	2.8	9.8	2.32

by a thick line ; corresponding elements in the different groups have been joined by dotted lines. The important correspondence between atomic volume and atomic number was brought out in 1870 by Lothar Meyer, and more recently relationships between κ and ν respectively with the atomic number have been demonstrated. The particular combination of these variables plotted in fig. 3 is of interest,

90 *Characteristic Vibration Frequency of an Element.*

since the expression represents an energy ratio, and considerations of energy have always proved a powerful method of attack in physical problems.

Fig. 3.



The form of the curve is seen to be periodic, following closely the Mendeleef classification. It will be noticed, in contrast with the atomic volume curves of Meyer, that the halogen elements form the peaks. This seems in agreement with the pronounced chemical activity of the halogen family. The alkali metals lie on a well-defined line, the elements above which are all non-metals and the elements below which, with one exception, all metals. The exception is silicon (Group III.), which lies on the line through Pb, Sn, and Ge. It will be noticed, too, that carbon does not lie on this line, as it should according to its place in the Periodic Table, but has a much higher position. In this connexion it would be interesting to know the position boron occupies on the curve.

It has not been found possible to insert values for the inert elements, but they will in all probability be very small, on account of the smallness of their vibration frequency, and also of their compressibility at very low temperatures.

In conclusion, I wish to thank my wife for the valuable assistance she gave me during the preparation of the paper.

University of Leeds,
Aug. 10, 1923.

VIII. *A Note on Mr. Ablett's Paper on the Angle of Contact between Paraffin Wax and Water.* By ALLAN FERGUSON, M.A., D.Sc. *

IN the August number of the *Philosophical Magazine*, Mr. R. Ablett describes a series of ingenious and important experiments which gives the contact angle between paraffin wax and water. He finds that, for various speeds of rise or fall of the water-air surface, the contact angle (θ) corresponding to a stationary meniscus is connected with the angles (θ_1) and (θ_2) corresponding respectively to a rising and to a falling meniscus by the relation $2\theta = \theta_1 + \theta_2$. For speeds of rise or fall greater than about 0.5 mm./sec., θ_1 and θ_2 remain constant, but the same law holds.

This result, which has been tested for contact angles in the neighbourhood of 90° only, will undoubtedly have important bearings on the application of surface-tension theories to industrial problems, and it is much to be desired that Mr. Ablett should extend his measurements to include *small* contact angles.

With a not unnatural enthusiasm, but without any experimental justification, he extrapolates his law down to small contact angles, and endeavours to explain certain well-known phenomena in terms of this law.

Thus, in discussing certain experiments which I described to the Faraday Society some time ago, he says:—"Allan Ferguson, in 'Studies in Capillarity—II.' (Faraday Soc. Trans. 1921), dealing with a method of adjusting the air-pressure to force the meniscus down to the level of the free liquid surface, says:—"The presence or absence of a constant error was tested by taking the mean of the readings (1) when the meniscus just disappeared within the tube, (2) when it just protruded from the tube. The mean of these pressures agreed satisfactorily with the "crucial" pressure."

"The results given in the present paper explain this. Taking for granted that $\theta_2 = 0$ for water, θ_1 finite but small, then as before, $T \cos \theta$ should agree with $\frac{1}{2}(T \cos \theta_1 + T \cos \theta_2)$."

In the first place it should be noted that Mr. Ablett misapprehends the method. The air-pressure is adjusted so as to force the meniscus down to the *lower end* of a vertical capillary plunged into the liquid, and to hold it there in a

* Communicated by the Author.

stationary state. This process avoids the necessity for calibrating the tube, and incidentally minimises errors due to adsorption at the walls of the capillary; simple as the modification may be, it is a very different matter from forcing the meniscus "down to the level of the free liquid surface." This, however, by the way.

Even if we admit the legitimacy of Mr. Ablett's extrapolation, I see no reason for assuming, as he does, that $T \cos \theta$ must be equal to the mean of $T \cos \theta_1$ and $T \cos \theta_2$, subject to the condition that θ_2 is zero and θ_1 small. Under these circumstances Mr. Ablett's equation $2\theta = \theta_1 + \theta_2$ reduces to $\theta_1 = 2\theta$; the equation

$$2 \cos \theta = \cos \theta_1 + \cos \theta_2$$

reduces under similar circumstances, unless my algebra is very far astray, to $\theta_1 = \theta\sqrt{2}$ —not at all in accordance with his premisses.

Similar remarks apply to his discussion of the experiments of Hartley and Bosanquet. These experimenters do not state the formula which they employ for evaluating the contact angle from measurements of a large sessile drop. Assuming that they treat the radius of the drop as very large—at best a risky matter—and use a formula of the type

$$1 + \cos \theta = \frac{\rho p h^2}{2T} = K h^2, \text{ say,}$$

where h is the total depth of the drop, it seems fairly obvious that Mr. Ablett's assumption [that under the circumstances of their experiment $\cos \theta = \cos \left(\frac{\theta_1 + \theta_2}{2} \right)$] leads to the result

that $h_1 + h_2/2h$ is *not* equal to unity. But as Mr. Ablett himself points out, $h_1 + h_2/2h$, as experimentally determined, *is* sensibly equal to unity. It would therefore seem that, as far as these experiments go, they point to a conclusion diametrically opposite to the one which he draws.

But this criticism is also incidental. The single and sufficient reason for rejecting Mr. Ablett's explanation is that it is not at all *ad rem*—and this on two counts. Mr. Ablett's experiments are essentially dynamical; the experiments which he discusses are statical in character. The symmetry of his own curves shows clearly that as the velocity decreases the angles θ_1 and θ_2 change *pari passu*, each approaching, from opposite sides, the stationary value θ , which is always symmetrically distant from corresponding

values of θ_1 and θ_2 . It would seem, therefore, that the correct interpretation of his results should be that a stationary meniscus should always occupy the same position in a tube whether it reach that position by rising or by falling. This is *not* in accordance with the experience of other workers—compare the quotation from Harkins and Brown's paper which is given by Mr. Ablett—and since his curves are extrapolated between zero and a velocity of 0.13 mm. per second, it seems desirable to carry out experiments at velocities between these limits in order to examine whether any tendency to asymmetry exists within this region.

Again, granting all his premisses, his explanation of the phenomena recorded in my paper only applies if one reading be taken with a falling, one with a rising meniscus, the crucial pressure being read with a stationary meniscus. Obviously these readings, made as they were merely to test the sensitiveness of the setting, were not taken in this highly artificial order. There is no suggestion of any such order in my text, neither were the readings taken with a moving meniscus. The obvious order of experiment, and the order in which the readings were taken, was:—the tube being immersed vertically in the liquid under test, the liquid rose in the tube. The liquid in the tube was then forced down until the meniscus was just short of appearing at the lower end (pressure head $h - \delta h$), then until it was just flush with the end (h), then until the end of the meniscus just protruded ($h + \delta h'$). *For each reading, the meniscus was held stationary.* The statement in my text simply asserts that $\delta h = \delta h'$ —or, to quote an analogous geometrical problem, in fixing accurately the position of a point on a curve it is possible to draw a chord so close to the tangent at the point that the chord intercepts equal arcs on each side of the point. It is a mere test of accuracy of setting and, with readings taken in this order, no question of contact angles arises.

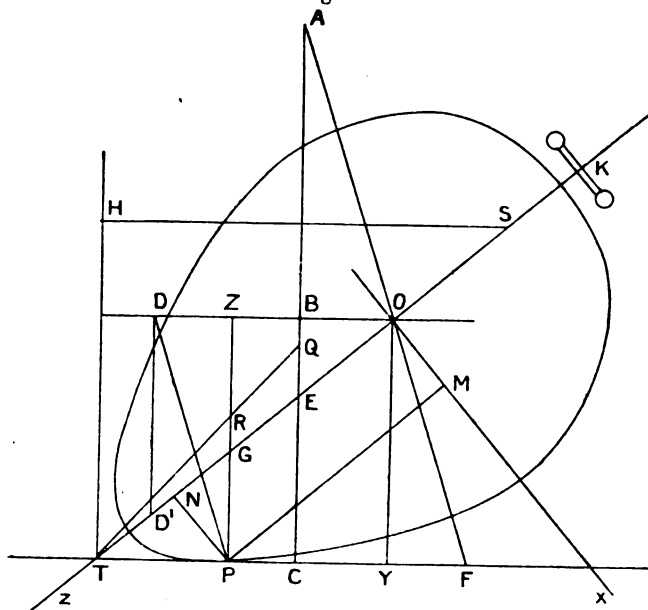
East London College,
Mile End Road, E. 1.
October, 1923.

IX. *Steady Precession of a Body rolling on a Table: with Slight Nutation superposed.* By Sir GEORGE GREENHILL *.

THE method in the Philosophical Magazine, March 1923, is extended here from the top, spinning about a fixed point, to the movement of a solid of revolution, free to wander in rolling under gravity on a horizontal table; shown off by a coin, plate, platter, canister, wine-glass, china egg, or any rounded solid body, not too large for an illustration of Terrestrial Dynamics, in an experiment within reach of all.

The treatment adopted is chosen again so as to dispense with the use of any method of approximation, and to proceed by demonstration of exact calculation.

Fig. 1.



1. Begin with the Steady Motion at a constant angle θ of the axis Oz to the vertical OY (fig. 1), where P the point of contact with the table describes a circle (radius b) round

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a centre C, and O the c.g. of the body describes another horizontal circle about a centre B, in the vertical line CB.

Produce CB up to A, where AB = λ is the height of the conical pendulum AO, revolving in the same period as a circuit of O.

The reaction S of the table will act through P parallel to OA, and the body being an M lb weight, the vertical component of S is M lb, and the moment of S about O is M.OB (ft.-lb), if S crosses the horizontal OB in D, a distance OD feet.

The axis Oz of the body crosses BC in a fixed point E, and EP is the instantaneous axis of rotation in the steady motion, with $OE = \frac{b}{\sin \theta}$; and then if P, R denote the components of angular velocity of the body about Ox, Oz,

$$\frac{R}{P} = \frac{EN}{NP} = \frac{z - \frac{b}{\sin \theta}}{x}, \text{ with } P = \mu \sin \theta, \quad (1)$$

if μ denotes the precessional velocity, so that

$$\frac{R}{\mu} = \frac{z \sin \theta - b}{x}; \text{ also } \lambda = \frac{g}{\mu^2}. \quad (2)$$

The components of angular momentum (A.M.) are then AP = $A\mu \sin \theta$ about Ox, and $h_3 = CR + K$ about Oz, the constant term K being added to allow for the A.M. of a flywheel K, on a smooth axle fixed in the axis Oz or parallel to it, forming part of the body.

Representing these components of A.M. vectorially to scale by kh and ho , so that Ok is the vector of resultant A.M., the velocity of k must be equated to the impressed couple, or with Og the vector component of A.M. about the vertical OY,

$$\mu \cdot gk = gM \cdot OD = \mu^2 \lambda \cdot OD, \quad (3)$$

$$\mu h_3 \sin \theta - \mu^2 A \sin \theta \cos \theta = M \mu^2 \lambda \cdot OD; \quad (4)$$

and denoting OY by p and YP by q , then

$$pb = \lambda \cdot YF, \quad pb + q\lambda = \lambda \cdot PF = \lambda \cdot OD, \quad (5)$$

$$\frac{h_3}{M\mu} = \frac{A}{M} \cos \theta + \frac{\lambda \cdot OD}{\sin \theta} = \frac{A}{M} \cos \theta + \frac{pb + q\lambda}{\sin \theta}. \quad (6)$$

Written as a quadratic in μ , with $b = z \sin \theta - \frac{R.x}{\mu}$,

$$\mu^2 \left(\frac{A}{M} \cos \theta + pz \right) - \mu \left(R \frac{p.x}{\sin \theta} + \frac{h_3}{M} \right) + \frac{gq}{\sin \theta} = 0, \quad (7)$$

$$\begin{aligned} & \left[2\mu \left(\frac{A}{M} \cos \theta + pz \right) - R \frac{p.x}{\sin \theta} - \frac{h_3}{M} \right]^2 \\ &= \left(\frac{R.p.x}{\sin \theta} + \frac{h_3}{M} \right)^2 - 4g \left(\frac{A}{M} \cos \theta + pz \right) \frac{q}{\sin \theta}, \quad (8) \end{aligned}$$

and the right-hand side must be positive, or vanishes in the critical state of Steady Motion, when the wobble begins.

Thus spun upright, with $p = z, x = 0$, but on a rounded end like an egg-shaped body, $\frac{p.x}{\sin \theta} = \rho$, the radius of curvature at the end, $\frac{q}{\sin \theta} = z - \rho$; and with $K = 0, h_3 = CR$ in a solid body, the wobble begins when

$$R^2 \left(z\rho + \frac{C}{M} \right)^2 = 4g \left(\frac{A}{M} + z^2 \right) (z - \rho) \quad (9)$$

and the critical energy is then

$$\frac{CR^2}{2g} = \frac{2C \left(\frac{A}{M} + z^2 \right) (z - \rho)}{\left(\frac{C}{M} + z\rho \right)^2}, \quad (10)$$

as in Routh's 'Advanced Rigid Dynamics,' p. 202.

2. In a general state of Unsteady Motion of the body, rolling about anyhow on the table, the equations are referred to moving axes in the figure 1, Ox, Oy, Oz , with U, V, W the components of linear velocity of O ; P, Q, R of angular velocity (A.V.) ; h_1, h_2, h_3 of A.M.; and $\theta_1, \theta_2, \theta_3$ the components of A.V. of the frame of reference $Oxyz$, not fixed in the body except that Oz is in coincidence with the axis of the body.

Then with x, y, z the coordinates of P the point of contact with the table; X, Y, Z the components (in absolute measure) of the reaction at P of the table on the body; α, β, γ the direction cosines of the downward vertical OY , normal to the table, the geometrical relations, expressing that the point of contact P is at rest for the moment on the table, are :

$$U - R\gamma + Qz = 0, \quad V - Pz + Rx = 0, \quad W - Qx + Py = 0. \quad (1)$$

The general dynamical equations are :

$$\frac{dU}{dt} - V\theta_3 + W\theta_2 = \frac{X}{M} + g \sin \theta, \quad (2)$$

$$\frac{dV}{dt} - W\theta_1 + U\theta_3 = \frac{Y}{M}, \quad (3)$$

$$\frac{dW}{dt} - U\theta_2 + V\theta_1 = \frac{Z}{M} + g \cos \theta, \quad (4)$$

$$\frac{dh_1}{dt} - h_2\theta_3 + h_3\theta_2 = yZ - zY, \quad (5)$$

$$\frac{dh_2}{dt} - h_3\theta_1 + h_1\theta_3 = zX - xZ, \quad (6)$$

$$\frac{dh_3}{dt} - h_1\theta_2 + h_2\theta_1 = xY - yX, \quad (7)$$

and the elimination of X, Y, Z , the reaction components, will lead to the differential equations of motion.

3. In our special case where the surface of the body is of revolution about Oz , and the body is kinetically symmetrical about Oz as a principal axis, we take Oy horizontal and the plane Oz, x through P the point of contact with the table; so that $y=0, \beta=0$; and eliminating at the outset the components of reaction, X, Y, Z ,

$$\frac{dh_1}{dt} - h_2\theta_3 + h_3\theta_2 + Mz \left(\frac{dV}{dt} - W\theta_1 + U\theta_3 \right) = 0, \quad . . . (1)$$

$$\frac{dh_2}{dt} - h_1\theta_2 + h_3\theta_1 - Mx \left(\frac{dV}{dt} - W\theta_1 + U\theta_3 \right) = 0, \quad . . . (2)$$

$$\begin{aligned} \frac{dh_2}{dt} - h_3\theta_1 + h_1\theta_3 - Mz \left(\frac{dU}{dt} - V\theta_3 + W\theta_2 \right) \\ + Mx \left(\frac{dW}{dt} - U\theta_2 + V\theta_1 \right) + gM(z\alpha - x\gamma) = 0. \end{aligned} \quad (3)$$

Denoting the Precession of the axes about the vertical by μ , variable in Unsteady Motion where the angle θ is variable between Oz and the downward vertical,

$$\left. \begin{aligned} \alpha &= \sin \theta, & \beta &= 0, & \gamma &= \cos \theta; \\ h_1 &= AP, & h_2 &= AQ, & h_3 &= CR + K. \end{aligned} \right\} . . . (4)$$

The constant K is added to allow for the influence of a flywheel on a smooth axle fixed in the body in the axis Oz ,

or parallel to it; and K remains constant during the motion although the axle changes in direction.

A large flywheel concealed in such a body is called a Gyrostat; it can be handled to feel the gyroscopic effect; or made useful on a large scale for controlling the rolling motion of a ship, or as in the Gyrocompass for steering it.

The axis Oz being fixed in the body, and the precession being reckoned clockwise on the table,

$$\theta_1 = P = \mu \sin \theta, \quad \theta_2 = Q = -\frac{d\theta}{dt}, \quad \theta_3 = \mu \cos \theta; \quad \dots \quad (5)$$

but θ_3 and R are different, because the frame of reference, $Oxyz$, rotates about Oz relatively to the body and independently.

With $y = 0$, the geometrical relations reduce to

$$U = -Qz, \quad V = Pz - Rx, \quad W = Qx. \quad \dots \quad (6)$$

Thus, with

$$P = \mu \sin \theta, \quad Q = -\frac{d\theta}{dt}, \quad \text{but } R \text{ not } \mu \cos \theta; \quad \dots \quad (7)$$

$$\theta_1 = P, \quad \theta_2 = Q, \quad \theta_3 = \mu \cos \theta; \quad \dots \quad (8)$$

$$h_1 = AP, \quad h_2 = AQ, \quad h_3 = CR + K; \quad \dots \quad (9)$$

and ρ denoting the radius of curvature PR of the meridian curve at P ,

$$\frac{dx}{dt} = -Q\rho \cos \theta, \quad \frac{dy}{dt} = 0, \quad \frac{dz}{dt} = Q\rho \sin \theta, \quad \dots \quad (10)$$

$$\begin{aligned} \frac{dV}{dt} - W\theta_1 + U\theta_3 &= \frac{d\mu}{dt} z \sin \theta - \frac{dR}{dt} x - 2Q\mu z \cos \theta \\ &\quad - Q\mu(x - \rho \sin \theta) \sin \theta + QR\rho \cos \theta, \end{aligned} \quad (11)$$

$$\begin{aligned} \frac{dU}{dt} - V\theta_3 + W\theta_2 &= -\frac{dQ}{dt} z + Q^2(x - \rho \sin \theta) \\ &\quad - \mu^2(z \sin \theta - x \cos \theta) \cos \theta, \end{aligned} \quad \dots \quad (12)$$

$$\begin{aligned} \frac{dW}{dt} - U\theta_2 + V\theta_1 &= \frac{dQ}{dt} x + Q^2(z - \rho \cos \theta) \\ &\quad + \mu^2(z \sin \theta - x \cos \theta) \sin \theta, \end{aligned} \quad \dots \quad (13)$$

$$\frac{dh_1}{dt} - h_2\theta_3 + h_3\theta_2 = A \frac{d\mu}{dt} \sin \theta - 2AQ\mu \cos \theta + Qh_3, \quad \dots \quad (14)$$

$$\frac{dh_2}{dt} - h_3\theta_1 + h_1\theta_3 = A \frac{dQ}{dt} + A\mu^2 \sin \theta \cos \theta - h_3\mu \sin \theta, \quad \dots \quad (15)$$

$$\frac{dh_3}{dt} - h_1\theta_2 + h_2\theta_1 = C \frac{dR}{dt}. \quad \dots \quad (16)$$

Introducing these values into (1) and (2),

$$\begin{aligned} A \frac{d\mu}{dt} \sin \theta - 2AQ\mu \cos \theta + Qh_3 + Mz \left[\frac{d\mu}{dt} z \sin \theta - \frac{dR}{dt} x \right. \\ \left. - 2Q\mu z \cos \theta - Q\mu(x - \rho \sin \theta) \sin \theta + QR\rho \cos \theta \right] = 0, \\ C \frac{dR}{dt} - Mx \left[\frac{d\mu}{dt} z \sin \theta - \frac{dR}{dt} x - 2Q\mu z \cos \theta \right. \\ \left. - Q\mu(x - \rho \sin \theta) \sin \theta + QR\rho \cos \theta \right] = 0, \\ \left(\frac{A}{M} + z^2 \right) \frac{d\mu}{dt} \sin \theta - xz \frac{dR}{dt} - Q\mu \left[2 \left(\frac{A}{M} + z^2 \right) \cos \theta \right. \\ \left. + (x - \rho \sin \theta) z \sin \theta \right] + QR\rho z \cos \theta + Q \frac{h_3}{M} = 0, \quad (17) \end{aligned}$$

$$\begin{aligned} \left(\frac{C}{M} + x^2 \right) \frac{dR}{dt} - xz \frac{d\mu}{dt} \sin \theta + Q\mu [(x - \rho \sin \theta)x \sin \theta \\ + 2xz \cos \theta] - QR\rho x \cos \theta = 0, \quad (18) \end{aligned}$$

two simultaneous differential equations (D.E.) of the first order for the determination of μ and R , or $CR + K = h_3$; thence two separate D.E.'s of the second order.

They are of intractable nature in general, although some cases are mentioned in the Report on Gyroscopic Theory, 1914 (R.G.T.), where the character is hyperelliptic or hypergeometrical, and so may be considered tractable to a certain extent.

4. The reduction of (3) § 3 leads to

$$\begin{aligned} \frac{dQ}{dt} \left(\frac{A}{M} + x^2 + z^2 \right) + Q^2 q \rho + \mu^2 \frac{A}{M} \sin \theta \cos \theta + \mu^2 p z \sin \theta \\ - \mu R p x - \mu \frac{h_3}{M} \sin \theta + g q = 0, \quad (1) \end{aligned}$$

with

$$z \cos \theta + x \sin \theta = p, \quad z \sin \theta - x \cos \theta = q = -\frac{dp}{d\theta},$$

so that

$$\begin{aligned} p - \frac{dq}{d\theta} = p + \frac{d^2 p}{d\theta^2} = \rho, \quad \frac{dq}{d\theta} = p - \rho, \\ \frac{dx}{d\theta} = +\rho \cos \theta, \quad \frac{dz}{d\theta} = -\rho \sin \theta. \end{aligned}$$

This equation (1), combined with (17), (18) § 3, will lead

to an equation—the Equation of Energy; and further integration is intractable.

But differentiating (1) with respect to θ , with $d\theta = -Qdt$, an equation is obtained in the general state of Unsteady Motion of the form

$$a_1 + b_1 \frac{d\mu}{\mu d\theta} \sin \theta + c_1 \frac{dR}{\mu d\theta} = 0, \quad (2)$$

$$a_1 = -\frac{d^2 Q}{\mu^2 Q d\theta^2} \left(\frac{A}{M} + x^2 + z^2 \right) + \frac{1}{\mu^2} \frac{d}{d\theta} (Q^2 q \rho) + \frac{A}{M} \cos 2\theta \\ + p z \cos \theta - q z \sin \theta - p \rho \sin^2 \theta \\ + \frac{R}{\mu} (q x - p \rho \cos \theta) - \frac{h_3}{M \mu} \cos \theta + \lambda (p - \rho), \quad . (3)$$

$$b_1 = 2 \frac{A}{M} \cos \theta + 2 p z - \frac{R}{\mu} \frac{p x}{\sin \theta} - \frac{h_3}{M \mu}, \quad (4)$$

$$c_1 = -\rho x - \frac{C}{M} \sin \theta. \quad (5)$$

Re-writing (17), (18) § 3 in the form

$$a_2 + b_2 \frac{d\mu}{\mu d\theta} \sin \theta + c_2 \frac{dR}{\mu d\theta} = 0, \quad (6)$$

$$a_3 + b_3 \frac{d\mu}{\mu d\theta} \sin \theta + c_3 \frac{dR}{\mu d\theta} = 0, \quad (7)$$

$$a_2 = 2 \left(\frac{A}{M} + z^2 \right) \cos \theta + (x - \rho \sin \theta) z \sin \theta - \frac{R}{\mu} z \rho \cos \theta - \frac{h_3}{M \mu}, \quad (8)$$

$$b_2 = \frac{A}{M} + z^2, \quad c_2 = -x z; \quad (9)$$

$$a_3 = -(x - \rho \sin \theta) x \sin \theta - 2 x z \cos \theta + \frac{R}{\mu} x \rho \cos \theta, \quad . . . (10)$$

$$b_3 = -x z, \quad c_3 = \frac{C}{M} + x^2; \quad (11)$$

the determinant $(a_1 \ b_2 \ c_3)$, result of the elimination of $\frac{d\mu}{\mu d\theta} \sin \theta$ and $\frac{dR}{\mu d\theta}$, as in Routh's 'Advanced Rigid Dynamics,' p. 192, will lead to the equation for $\frac{d^2 Q}{Q d\theta^2}$ requiring an integration of the previous equations.

Here is an exact equation of the general Unsteady Motion in an Antepenultimate State.

But these considerations, a contribution more to Scientific Method than advance of Scientific Thought, would lead us far beyond our scope, limited to the investigation of the Precession in Steady Motion, and a small Nutation superposed.

5. Restricted to our scope of Steady Precessional Motion at a constant inclination θ , with a small Nutation superposed, to assure the Stability, so that Q and $\frac{dQ}{dt}$ are zero, but $\frac{1}{Q} \frac{d^2Q}{d\theta^2} = -m^2$, then from (1) . . . (5) § 1,

$$a_1 = \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) - \left(\frac{A}{M} + z^2 \right) \sin^2 \theta + z^2 + xz \cos \theta - b\gamma - \frac{\rho^2}{x} (p \sin \theta - b \cos \theta) - (pb + q\lambda) \cot \theta + \lambda(\rho - p), \quad (1)$$

$$b_1 = \frac{A}{M} \cos \theta + pz - \frac{q\lambda}{\sin \theta}, \quad (2)$$

$$c_1 = -\frac{C}{M} \sin \theta - px, \quad (3)$$

$$\begin{aligned} a_2 &= 2 \left(\frac{A}{M} + z^2 \right) \cos \theta + (x - \rho \sin \theta) z \sin \theta \\ &\quad - \frac{z}{x} (z \sin \theta - b) \rho \cos \theta - \frac{A}{M} \cos \theta - \frac{\rho b + q\lambda}{\sin \theta} \\ &= \left(\frac{A}{M} + z^2 \right) \cos \theta + \frac{z}{x} \{ p(x - \rho \sin \theta) + b\rho \cos \theta \} - \frac{\rho b + q\lambda}{\sin \theta}, \\ b_2 &= \frac{A}{M} + z^2, \quad c_2 = -xz. \quad (4) \end{aligned}$$

$$\begin{aligned} a_3 &= -(x - \rho \sin \theta) x \sin \theta - 2xz \cos \theta + (z \sin \theta - b) \rho \cos \theta \\ &= -xz \cos \theta - p(x - \rho \sin \theta) - b\rho \cos \theta, \\ b_3 &= -xz, \quad c_3 = \frac{C}{M} + x^2. \quad (5) \end{aligned}$$

Write D for $\left(\frac{A}{M} + z^2 \right) \left(\frac{C}{M} + x^2 \right) - x^2 z^2$; and then from (4), (5) § 4,

$$\begin{aligned} D \frac{d\mu}{\mu d\theta} \sin \theta &= -2D \cos \theta - \frac{C}{M} (x - \rho \sin \theta) z \sin \theta \\ &\quad + \frac{R}{\mu} \frac{C}{M} \rho \cos \theta + \left(\frac{C}{M} + x^2 \right) \frac{h_3}{M\mu} \\ &= -D \cos \theta - \frac{C}{M} \frac{z}{x} [p(x - \rho \sin \theta) + b\rho \cos \theta] \\ &\quad + \left(\frac{C}{M} + z^2 \right) \frac{bp + q\lambda}{\sin \theta} \\ &= -D \cos \theta - \frac{C}{M} z \cdot BQ + \left(\frac{C}{M} + z^2 \right) \frac{\rho b + q\lambda}{\sin \theta}. \quad (6) \end{aligned}$$

$$\begin{aligned}
 D \frac{h_3}{\mu \sin \theta} &= \frac{A}{M} (x - \rho \sin \theta) x \sin \theta - \frac{R}{\mu} \frac{A}{M} x \rho \cos \theta + \frac{h_3}{M \mu} x z \\
 &= \frac{A}{M} \{ p(x - \rho \sin \theta) + b \rho \cos \theta \} + x z \frac{p b + q \lambda}{\sin \theta} \\
 &= + \frac{A}{M} x \cdot R Q + x z \frac{p b + q \lambda}{\sin \theta} \dots \dots \dots (7)
 \end{aligned}$$

(λ.O.D.)

This is with R and h_3 exterminated; but retaining them and exterminating b , when we wish to obtain Routh's result for a disk.

Here $p(x - \rho \sin \theta) + b \rho \cos \theta = x \cdot BQ, \dots \dots (8)$

if TR produced through R the centre of curvature cuts BC in Q in fig. 1; and then

$$\begin{aligned}
 a_1 &= \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) - \frac{A}{M} \sin^2 \theta - p^2 - b q + p z \cos \theta \\
 &\quad - q \lambda \cot \theta + \lambda(p - c) - (p b + q \lambda) \cot \theta + p \cdot BQ, \quad (9)
 \end{aligned}$$

$$a_2 = \left(\frac{A}{M} + z^2 \right) \cos \theta - \frac{p b + q \lambda}{\sin \theta} + z \cdot BQ, \dots \dots \dots (10)$$

$$a_3 = -x z \cos \theta - x \cdot BQ, \dots \dots \dots (11)$$

$$\begin{aligned}
 a_1 - a_2 \cos \theta + a_3 \sin \theta &= \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) - \frac{A}{M} - p^2 - b q - q \lambda \cot \theta \\
 &\quad + \lambda(p - \rho) + p \cdot BQ. \quad (12)
 \end{aligned}$$

Then the determinant of § 4

$$\begin{aligned}
 a_1(b_2 c_3 - b_3 c_2) + a_2(b_3 c_1 - b_1 c_3) + a_3(b_1 c_2 - b_2 c_1) \\
 = D(c_1 - a_2 \cos \theta + a_3 \sin \theta) \\
 + \frac{q \lambda}{\sin \theta} \left[\left(\frac{C}{M} + x^2 \right) a_2 + x z a_3 \right] = 0, \quad (13)
 \end{aligned}$$

and

$$\begin{aligned}
 \left(\frac{C}{M} + x^2 \right) a_2 + x z a_3 &= \left(\frac{C}{M} + x^2 \right) \left[\left(\frac{A}{M} + x^2 \right) \cos \theta + z \cdot BQ - \frac{p b + q \lambda}{\sin \theta} \right] \\
 &\quad - x^2 z^2 \cos \theta - x^2 z \cdot BQ \\
 = D \cos \theta + \frac{C}{M} z \cdot BQ - \left(\frac{C}{M} + x^2 \right) \frac{p b + q \lambda}{\sin \theta} \dots \dots \dots (14)
 \end{aligned}$$

The minor determinants of $(a_1 b_2 c_3)$ in § 4 are :

$$\begin{aligned} b_2 c - b_3 c_2 &= D, \\ b_3 c_1 - b_1 c_3 &= -D \cos \theta + \left(\frac{C}{M} + x^2 \right) \frac{q\lambda}{\sin \theta}, \\ b_1 c_2 - b_2 c_1 &= D \sin \theta + xz \frac{q\lambda}{\sin \theta}; \quad . \quad . \quad (15) \end{aligned}$$

and so the complete determinant is

$$D(a_1 - a_2 \cos \theta + a_3 \sin \theta) + \left[\left(\frac{C}{M} + x^2 \right) a_2 + xz a_3 \right] \frac{q\lambda}{\sin \theta}, \quad (16)$$

leading to the simple equation for $\frac{m^2}{\mu^2}$ or $\frac{\lambda}{L}$,

$$\begin{aligned} \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) D &= D \left(\frac{A}{M} + p^2 + bq - q\lambda \cot \theta \right) - D\lambda(p - \rho) \\ &\quad - \frac{C}{M} z \cdot BQ \frac{q\lambda}{\sin \theta} + \left(\frac{C}{M} + x^2 \right) \frac{pb + q\lambda}{\sin \theta} \cdot \frac{q\lambda}{\sin \theta}, \quad (A) \end{aligned}$$

involving geometrical lengths only, as g has been exterminated by the introduction of an E.S.P. (equivalent in simple pendulum) length $\lambda = \frac{g}{\mu^2}$, $L = \frac{g}{m^2}$ fundamental in our subject.

Then $\frac{A}{M}, \frac{C}{M}$ can be measured experimentally by swinging the body as a pendulum about the axis PN, PM, and noting the length of the E.S.P. l_1, l_3 , making

$$\frac{A}{M} + z^2 = l_1 z, \quad \frac{C}{M} + x^2 = l_3 x, \quad D = xz(l_1 l_3 - xz); \text{ also}$$

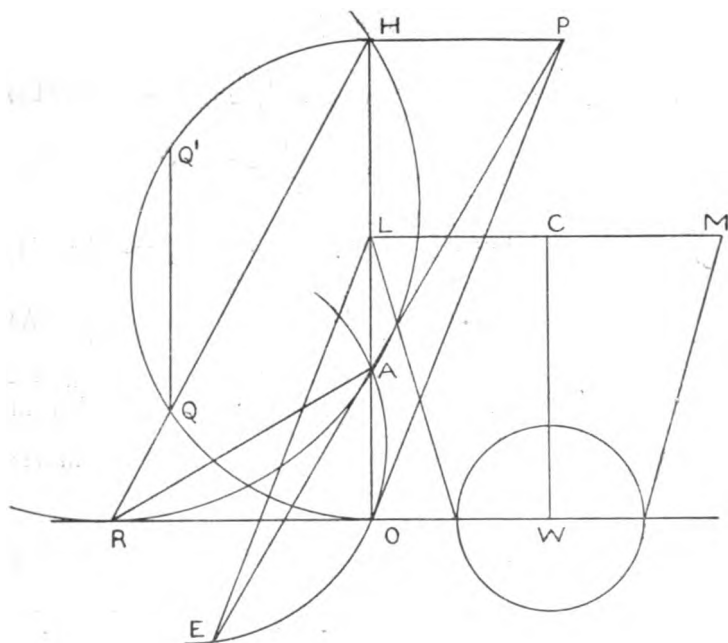
$\frac{A}{M} + x^2 + z^2 = l \cdot OP$, by swinging the body about an axis through P parallel to Oy.

The result is independent of the local g , or density of the body, so that the determinant is a relation between algebraical symbols of length only. No time measurement required and no unit of weight or weighing, as the density does not intervene.

To make a simple pendulum to measure l the length of the E.S.P. with accuracy, take a sphere W with a diametral hole, and pass a fine smooth thread through it,

supported at the ends L and M in fig. 2 at the same level ; then l will be exactly the depth of the centre W below LM, the thread being smooth enough not to turn the sphere, oscillating bodily without rotation. And l is adjusted to the desired length by drawing the ends L and M

Fig. 2.



apart, while the sphere can be enlarged to any size desirable, in visible oscillation ; not the invisible particle postulated in the ordinary text-book.

The method is suitable for a problem of Terrestrial Dynamics, not beyond the scope of the human race imprisoned on the surface of the Earth, capable only of theoretical ideas of Celestial Dynamics, in the description of Socrates according to Plato, in *Phædo*.

But all matter is transparent to gravity, and suggestions arise here for a repetition of the Cavendish experiment with this simple pendulum.

Expressed in (A) by powers of $\frac{q\lambda}{\sin \theta}$, and $b\}$ replaced by $z \sin \theta - \frac{R}{\mu} x$,

$$\begin{aligned} & \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) D \\ = & D \left(\frac{A}{M} + p^2 + q^2 \right) - D\lambda(p - \rho) - \left[D \cos \theta + \frac{C}{M} \cdot ON \cdot BQ \right. \\ & \left. - \left(\frac{C}{M} + x^2 \right) \rho \left(z - \frac{R}{\mu} \frac{x}{\sin \theta} \right) \right] \frac{q\lambda}{\sin \theta} + \left(\frac{C}{M} + x^2 \right) \left(\frac{q\lambda}{\sin \theta} \right)^2. \end{aligned} \quad \dots (B)$$

6. The body can roll round in a circle with the axis horizontal when it has bias, so that z is not zero, and then $\theta = \frac{1}{2}\pi$, $p = x$, $q = z$, $\frac{R}{\mu} = \frac{z - b}{x}$, $BQ = x - \rho$, as BQ is horizontal; and then in (A),

$$\begin{aligned} \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) D = & D \left(\frac{A}{M} + x^2 + bz \right) - D\lambda(x - \rho) \\ & - \frac{C}{M} z(x - \rho)z\lambda + \left(\frac{C}{M} + x^2 \right) (bx + z\lambda)z\lambda. \end{aligned} \quad (1)$$

With no bias, $z = 0$, $\mu = 0$, and the path over the table is straight, with a slight sinuosity, where in (A), (B),

$$m^2 \left(\frac{A}{M} + x^2 \right) = \frac{h_3}{A} \left(Rx + \frac{h_3}{M} \right) - g(x - \rho). \quad \dots (2)$$

As a solid body, with $K = 0$, $h_3 = CR$,

$$\frac{m^2}{R^2} \left(\frac{A}{M} + x^2 \right) = \frac{C}{A} \left(\frac{C}{M} + x^2 \right) - \frac{g}{R^2} (x - \rho), \quad \dots (3)$$

and there are m sinuosities in R revolutions.

As a Kelvin gyrostat, a flywheel concealed in a cover with a sharp edge, placed on the table the body can hold itself upright with the axle horizontal and $\mu = 0$, $R = 0$; stationary apparently except for a slight imperceptible oscillation,

swaying $\frac{m}{\pi}$ times per second, where

$$m^2 = \frac{\frac{K^2}{MA} - g(x - \rho)}{\frac{A}{M} + x^2}, \quad \dots \quad (4)$$

if the flywheel is spun with A.M. K ; and m^2 must be positive for this upright position to be stable.

So too for a solid body like a biscuit or curtain-ring, spun about a vertical diameter with A.V. μ ,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) = \frac{A}{M} + x^2 - \lambda(x - \rho) \quad \dots \quad (5)$$

and the energy $\frac{A\mu^2}{2g}$ must then exceed $\frac{\frac{1}{2}M(x - \rho)}{1 + \frac{Mx^2}{A}}$ for the stability of the motion.

Spinning upright on one end, with $\theta = 0$, $x = 0$, but $\frac{x}{\sin \theta} = PG = \rho$, $\frac{g}{\sin \theta} = OG = z - \rho$, $p = z$, $D = \frac{C}{M} \left(\frac{A}{M} + z^2 \right)$, $BQ = p \left(1 - \rho \frac{\sin \theta}{x} \right) + \rho \left(z \frac{\sin \theta}{x} - \frac{R}{\mu} \right) = z - \frac{R}{M\rho} = \frac{b}{\sin \theta}$, with $b = 0$; and dividing out $\frac{C}{M}$,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + z^2 \right)^2 = \left[\frac{A}{M} + z^2 - \lambda(z - \rho) \right]^2 \quad \dots \quad (6)$$

With the Steady Motion condition of § 1, and $h_3 = CR$,

$$\frac{g\lambda}{\sin \theta} = \lambda(z - \rho) = \frac{h_3}{M\mu} - \frac{A}{M} - \frac{p\lambda}{\sin \theta} = \left(\frac{C}{M} + z\rho \right) \frac{R}{\mu} - \frac{A}{M} - z^2, \quad \dots \quad (7)$$

$$\frac{m}{\mu} = \frac{\frac{A}{M} + z^2 - \lambda(z - \rho)}{\frac{A}{M} + z^2} = \frac{2 \left(\frac{A}{M} + z^2 \right) - \left(\frac{C}{M} + z\rho \right) \frac{R}{\mu}}{\frac{A}{M} + z^2}, \quad \dots \quad (8)$$

$$\frac{m}{R} = \frac{2 \frac{\mu}{R} \left(\frac{A}{M} + z^2 \right) - \frac{C}{M} - z\rho}{\frac{A}{M} + z^2} = \frac{\frac{C}{M} + z\rho}{\frac{A}{M} + z^2} \cdot \frac{\frac{A}{M} - \lambda(z - \rho)}{\frac{A}{M} + \lambda(z - \rho)}; \quad (9)$$

and the axis oscillates, swaying slightly to and fro, m times in R revolutions of the body.

In the special case where the centre O is at rest, $b=0$, as in Routh, ex. 2, p. 197, for the disk, and OP is the axis of instantaneous rotation, $\frac{R}{\mu} = \frac{z}{x} \sin \theta$, $x \cdot BQ = p(x - \rho \sin \theta)$,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) D = D \left(\frac{A}{M} + p^2 \right) - D\lambda(p - \rho) - Dq\lambda \cot \theta \\ - \frac{C}{M} z p \left(1 - \frac{\rho}{x} \sin \theta \right) \frac{q\lambda}{\sin \theta} + \left(\frac{C}{M} + x^2 \right) \left(\frac{q\lambda}{\sin \theta} \right)^2, \quad (10)$$

and in the Steady Motion condition,

$$\frac{q\lambda}{\sin \theta} = \frac{h_3}{M\mu} - \frac{A}{M} \cos \theta. \quad (11)$$

Then for the disk of Routh, $z=0$, $p=x \sin \theta$, $q=-x \cos \theta$, $R=0$, $h_3=0$, $\frac{A}{M} = \frac{\lambda x}{\sin \theta}$, $\lambda x = \frac{A}{M} \sin \theta$,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) = \frac{A}{M} + x^2 \sin^2 \theta + \lambda x \frac{\cos^2 \theta}{\sin \theta} \\ - \lambda x \sin \theta + \frac{\frac{C}{M} + x^2}{D} \lambda^2 x^2 \cot \theta \\ = \frac{A}{M} + x^2 \sin^2 \theta + \frac{A}{M} \cos^2 \theta - \frac{A}{M} \sin^2 \theta + \frac{A}{M} \cos^2 \theta \\ = 3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta, \quad (12)$$

$$L = \frac{g}{m^2} = \frac{A}{Mx} \cdot \frac{\left(\frac{A}{M} + x^2 \right) \sin \theta}{3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta}, \quad (13)$$

in agreement with Routh.

7. Tested for the previous case in Phil. Mag. March 1923 of the spinning top on a sharp point, $\rho=0$, in which K can be lumped up with CK in h_3 ,

$$x=0, \quad b=q=z \sin \theta, \quad p=z \cos \theta, \quad BQ=0, \quad D = \frac{C}{M} \left(\frac{A}{M} + z^2 \right);$$

and dividing out $\frac{C}{M}$,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + z^2 \right)^2 = \left(\frac{A}{M} + z^2 \right)^2 - 2 \left(\frac{A}{M} + z^2 \right) z \lambda \cos \theta + z^2 \lambda^2. \quad (1)$$

Then, as in *Phil. Mag.* July 1922, p. 387, with O at the point of the top in a small smooth cup, and $OP=l$, $l_z = \frac{A}{M} + z^2$, $OA=\lambda$, drawn vertically upward in the figure there;

$$\frac{m^2}{\mu^2} = \frac{\lambda}{L} = 1 - 2 \frac{\lambda}{l} \cos \theta + \frac{\lambda^2}{l^2} = \frac{AP^2}{OP^2}, \quad \dots \quad (2)$$

and the nutations of the axle are to the circuits round the vertical in the ratio of AP to OP.

To cut off on OA the length OL=L, describe the circle AOE through O and A touching OP at O, and crossing PA in E; then EL parallel to OP will cut off OL. For

$$\frac{OP^2}{AP^2} = \frac{AP \cdot PE}{AP^2} = \frac{PE}{AP} = \frac{OL}{OA}, \quad \dots \quad (3)$$

as required.

In the Steady Motion of the top round the vertical,

$$\begin{aligned} \frac{CR\mu}{M} &= \mu^2 \frac{A}{M} \cos \theta + g \cdot OG \\ &= \mu^2 \frac{A}{M} \cos \theta + n^2 \cdot OG \cdot OP = \frac{A}{M} (\mu^2 \cos \theta + n^2), \quad (4) \end{aligned}$$

$$\frac{CR}{An} = \frac{\mu}{n} \cos \theta + \frac{n}{\mu}; \quad \dots \quad (5)$$

and taking $n^2 = p^2 \cos \theta$, $\frac{\mu^2}{n^2} = \frac{OP}{OA}$, $\frac{\mu^2}{p^2} = \frac{OH}{OA}$,

$$\frac{\mu}{p} + \frac{p}{\mu} = \sqrt{\frac{OH}{OA}} + \sqrt{\frac{OA}{OH}} = \cot \alpha + \tan \alpha = \sin 2\alpha, \quad (6)$$

$$\text{with } \sin 2\alpha = \frac{2Ap}{CR}, \quad \frac{OH}{OA} = \tan \alpha.$$

Then if QQ' is drawn vertical in fig. 2 to cross the circle on OH in Q, Q', at a distance from AH in the ratio to OH of 2Ap to CR, and HQ is produced to meet the horizontal through O in R, the circle through R and H touching OR

at R will cut off a length OA, and make the angles ORA and OHR equal.

The same method can be extended to the rolling body of § 1; and there in fig. 1, with

$$\frac{A}{M} = OE \cdot OS, \quad g = n^2 \cdot OS = p^2 \cdot OH, \quad \dots \quad (7)$$

the Steady Motion condition can be written

$$\frac{\mu}{p} + \frac{p}{\mu} = \frac{h_3}{Ap}, \quad \dots \quad (8)$$

with the same geometrical construction for $\lambda = AB$.

But there does not appear to be any similar geometrical interpretation of $L = \frac{g}{m^2}$ for the nutation.

8. For a sharp edge, as of a coin, canister, wine-glass, put $\rho = 0$; but this does not introduce much simplification in the general case.

If, however, $z = 0$ as well, we have the case of a disk rolling on a plane, discussed by Routh in his ex. 3, p. 197; and then

$$p = x \sin \theta, \quad q = -x \cos \theta, \quad D = \frac{A}{M} \left(\frac{C}{M} + x^2 \right), \quad \dots \quad (1)$$

and dividing out $\frac{C}{M} + x^2$ in (A) § 5,

$$\begin{aligned} & \frac{m^2}{\mu^2} \frac{A}{M} \left(\frac{A}{M} + x^2 \right) \\ &= \frac{A}{M} \left(\frac{A}{M} + x^2 \sin^2 \theta - bx \cos \theta + \lambda x \frac{\cos^2 \theta}{\sin \theta} - \lambda x \sin \theta \right) \\ & \quad - \frac{bx \sin \theta - \lambda x \cos \theta}{\sin \theta} \cdot \frac{\lambda x \cos \theta}{\sin \theta}, \quad \dots \quad (2) \end{aligned}$$

with

$$\lambda x \cot \theta = \frac{A}{M} \cos \theta - \left(\frac{C}{M} + x^2 \right) \frac{R}{\mu},$$

$$bx - \lambda x \cot \theta = -\frac{A}{M} \cos \theta + \frac{CR}{M\mu}, \quad \frac{b}{x} = -\frac{R}{\mu}, \quad \dots \quad (3)$$

and then

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) = \frac{A}{M} (1 + 2 \cos^2 \theta) + x^2 \sin^2 \theta - \frac{R}{\mu} \cos \theta \left(3 \frac{C}{M} + x^2 \right) + \frac{C}{A} \left(\frac{C}{M} + x^2 \right) \frac{R^2}{\mu^2} - \frac{gx}{\mu^2} \sin \theta, \quad (4)$$

in agreement with Routh, when $C=2A$, in the thin disk.

But in Routh's result there is a redundancy of quantities; so replacing

$$\frac{gx \sin \theta}{\mu^2} = \lambda x \sin \theta \text{ by } \frac{A}{M} \sin^2 \theta - \frac{R}{\mu} \left(\frac{C}{M} + x^2 \right) \frac{\sin^2 \theta}{\cos \theta}, \quad (5)$$

$$\begin{aligned} \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) &= 3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta \\ &\quad - \left[\frac{C}{M} (4 \cos \theta - \sec \theta) + x^2 (2 \cos \theta - \sec \theta) \right] \frac{R}{\mu} \\ &\quad + \frac{C}{A} \left(\frac{C}{M} + x^2 \right) \frac{R^2}{\mu^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6) \end{aligned}$$

Then, in Routh's example 2, p. 197, where $b=0$, $R=0$,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) = 3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta, \quad . \quad . \quad . \quad . \quad (7)$$

$$\begin{aligned} m^2 &= \frac{g M x}{A} \frac{3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta}{\left(\frac{A}{M} + x^2 \right) \sin \theta}, \\ L &= \frac{A}{M x} \frac{\left(\frac{A}{M} + x^2 \right) \sin \theta}{3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta}, \quad . \quad . \quad . \quad . \quad (8) \end{aligned}$$

in agreement, for $\frac{m}{\pi}$ beats per second.

X. *The Molecular Association of Liquids and Highly-Compressed Gases.*—Parts I. and II. By E. E. WALKER, D.Sc., D.I.C., A.C.G.I.*

PART I.—MOLECULAR ASSOCIATION AT THE CRITICAL POINT.

THE determination of the degree of molecular association of liquids presents considerable difficulties because the laws governing the properties of liquids are very imperfectly understood. It is on this account that most methods of determining the association factor of liquids depend directly or indirectly on the law of corresponding states, which is itself only a rough approximation. Unfortunately, errors much larger than those due to the inaccuracy of this law are generally introduced by neglecting the fact that the critical pressure and temperature to which an associated liquid at the temperature T should be referred are *not* the observed critical constants, but those which would have been observed if the substance had been raised from the temperature T to the critical point without any change in the degree of association taking place. Batschinski† recognized this fact, but his method of determining this hypothetical critical temperature does not appear to have been very satisfactory, and the modification of the Eötvös equation to which his theories led him gave unsatisfactory results.

In this series of papers the author proposes to study the effect of molecular size on the critical constants, and to use the knowledge thus obtained to calculate the association factor of liquids from a modified law of corresponding states.

According to van der Waals's equation the critical temperature is proportional to $\frac{a}{b}$. If we assume that the molecular attractive power " a " and the molecular volume " b " are doubled when one molecule combines with another of the same sort to form a double molecule, then the critical temperature should remain unaffected. This is contrary to all accepted belief, and there can be no doubt at all that the boiling-point and critical point are, in fact, raised by molecular association. Since the space occupied by the double molecule must be practically double that occupied by the single molecule, we are driven to the conclusion either that

* Communicated by the Author.

† A. Batschinski, *Zeit. Phys. Chem.* lxxv. p. 665 (1911), and lxxxii. pp. 86 and 90 (1913); for another method see xl. p. 629 (1902).

the molecular attractive power is increased by combination or that van der Waals's equation misrepresents the facts. The first alternative seems improbable, and, since van der Waals's equation is known to be inaccurate at the critical point, the second alternative has been accepted. On this account, and in order to explain a variety of phenomena, the following modified equation of state has been adopted :

$$\left(P + \frac{a}{V^{2/3}}\right)(V-b) = RT. \quad \dots \quad (1)$$

This equation was first suggested by P. de Heen in 1887, and has been examined by Dieterici and others*. It has the advantage of being very much more accurate than van der Waals's equation in the neighbourhood of the critical point, but it fails for gases under moderate pressures. According to this equation the value of the critical coefficient $\frac{RT_c}{P_c V_c}$ should be 3.75, and this was the mean value found by Young for a number of organic compounds, while van der Waals's equation requires that it should have a value of 2.5.

The author was led to adopt Dieterici's equation in the first place because the values of "a" calculated from the critical constants by its means were found to be nearly additive†, *e. g.*, the homologous increment was nearly constant in a given series. At the present stage the selection of this equation may be justified by the fact that, since the critical temperature is proportional to $\frac{a}{b^{2/3}}$, the doubling of *a* and *b* by association leads to a higher critical temperature, a conclusion which is more in accordance with the facts than that deduced from van der Waals's equation.

In equation (1) *V* represents the volume of a gram molecule. If the substance is associated the size of the molecule is not known, but we may substitute $n_c V$ for *V* and define *V* as the volume of a gram formula weight, n_c being the association factor at the critical point. Solving for n_c we get

$$n_c = \frac{4}{15} \frac{RT_c}{P_c V_c} \quad \dots \quad (2)$$

* See Ostwald's *Handbuch der Allgemeinen Chemie*, vol. iii. p. 344.

† H. van Laar finds that *b* and $\sqrt{a}$ determined from the critical constants by van der Waals's equation are approximately additive. These relationships are not sufficiently accurate for the purpose of the present investigation. *Journ. Chem. Phys.* xiv. p. 3; xvi. p. 411; xviii. p. 273.

But the critical coefficient $\frac{RT_c^*}{P_c V_c}$ is not quite constant even for substances such as the paraffins, which are usually considered to be unassociated so that $n_c = 1$. Guye and Walden both regard this critical coefficient as a function of the critical temperature, but the present author finds that it can be represented much more accurately as a function of the length of the molecule. Thus, for instance, the critical coefficient of di-iso-butyl is (3·810), a value closer to that for hexane (3·83), which has the same length of molecule, than to that for octane (3·865), with which it is isomeric. The critical coefficients of isopentane (3·735) and di-isopropyl (3·741), which have the same length of molecule, are almost equal and smaller than the value for pentane (3·766). Very short molecules, such as methane (3·46) and hydrogen (3·27), have correspondingly small critical coefficients. These relationships are almost entirely obscured if we regard this critical coefficient as a function of the critical temperature.

If in equation (1) we introduce a function of the length "l" of the molecule thus :

$$\left(P + \frac{a}{(n_c V)^{5.3}} \right) (n_c V - b) = RT \times \frac{1}{f(l)}, \quad \dots (3)$$

we get for " n_c "

$$n_c = \frac{4}{15} \frac{RT_c}{P_c V_c} \times \frac{1}{f(l)}, \quad \dots (4)$$

where $f(l) = 0.838 + 0.174 \log l$.

This function of "l" has been so chosen that " n_c " is as nearly as possible unity for the saturated paraffins.

The length of the molecule is estimated by means of a few simple conventions from the following atomic diameters :—

Hydrogen	0.75
Oxygen	1.30
Nitrogen	1.30
Carbon.....	1.54
Fluorine	1.35
Chlorine	2.10
Bromine	2.38
Iodine	2.80
Tin	2.80

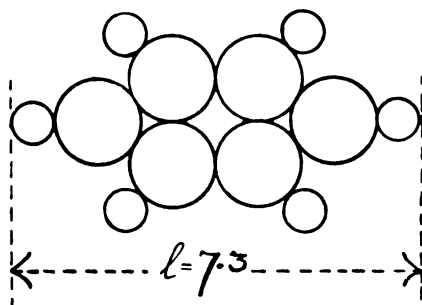
With the exception of hydrogen these are the usually accepted atomic diameters. Further research and a more

* S. Young correlated abnormal values of this quantity and molecular association, and the relationship has been generally accepted.

accurate evaluation of $f(l)$ may render it possible to use the normal atomic diameter of this element. The length of a molecule is taken as the sum of the atomic diameters in the longest chain, shorter side chains being neglected entirely. The molecules are therefore regarded as being stretched out to their greatest length, no account being taken of zig-zag or spiral formations. In this way we get the following values of " l ":—

Methane	1 carbon atom + 2 hydrogen atoms	$l=3.04$
Butane	4 carbon atoms + 2 hydrogen atoms	$l=7.66$
Pentane	5 carbon atoms + 2 hydrogen atoms	$l=9.20$
Iso-pentane	4 carbon atoms + 2 hydrogen atoms	$l=7.66$
Ethyl alcohol	2 carbon atoms + 2 hydrogen atoms + 1 oxygen atom	$l=5.88$

This convention breaks down when estimating the length of molecules containing a ring structure. It is found, however, that in order to make " n_c " equal to unity for the saturated ring compound hexamethylene one must assume a length of 7.3. This is in accordance with spatial considerations, if we assume that the ring is stretched out to its greatest length, as in the case of straight chain molecules. The ring might be pictured thus:—



This conception indicates that meta- and ortho-di-derivatives will be shorter than the corresponding para-di-derivative.

It seems reasonable to suppose that when two molecules associate to form one, the double molecule thus formed will have twice the length of the single molecule. Ordinary chemical considerations, supported by the work of Langmuir and others on surface films, suggest that in the case of primary substitution products the point of attachment would be the terminal group. If this is so, the average length of

the molecule of an associated substance will be greater than that found by the conventional method just described. One might get over this difficulty by substituting $n \times l$ for l in equation (4), but this leads to an expression which is difficult to solve. The correction is in any case small, and one may use the following approximation:—

$$n_c^{1+x} = \frac{4}{15} \frac{RT_c}{P_c V_c} \times \frac{1}{f(l)}, \quad \dots \dots (4a)$$

where x is equal to $-\frac{\log \frac{f(2l)}{f(l)}}{\log 2}$. This gives accurate results when $n=1$ and when $n=2$. For intermediate values of n it is a satisfactory approximation. It could not be used if n_c were appreciably greater than 2, but no association factor greater than 1.5 has been found at the critical point up to the present.

Values of n_c calculated from (4a) are recorded in Table I. Values of $\frac{4}{15} \frac{RT_c}{P_c V_c}$ are given for comparison in order to show just what influence the introduction of $f(l)$ into the expression exerts on the values of " n_c ". Deviations from unity in the case of normal saturated paraffins may be regarded as due to inaccuracies in the evaluation of $f(l)$. It is not maintained that the saturated paraffins are absolutely free from double molecules, but it is believed that they are at most only very slightly associated. The method adopted here is to determine the association factor of an organic compound in terms of that of a saturated paraffin having the same length of molecule. The basis of the method rests, therefore, on the carbon skeleton, and it must be applied with caution to purely inorganic substances. On the other hand, the association factors calculated for the inorganic substances hydrogen, oxygen, nitrogen, water, ammonia, hydrogen chloride, and stannic chloride appear to be reasonable and in accordance with what one might expect from the general properties of these substances. The results recorded in the table will be discussed in another communication, when the association factors have been determined at temperatures other than the critical. It may be pointed out, however, that the results are in general agreement with those given by Guye's molecular refraction method, but are free from certain anomalies which indicate that Guye's method is not reliable.

TABLE I.

Substance.	<i>l</i> .	$\frac{4}{15} \frac{RT_c}{P_c V_c}$	<i>n_c</i> .
Hydrogen	1.5	0.872	1.003
Oxygen	2.6	0.912	1.002
Nitrogen	2.6	0.912	1.002
Carbon dioxide	4.14	0.957	1.012
Methane	3.04	0.923	1.001
Ethane	4.58	0.947	0.994
Pentane	9.20	1.004	0.998
Hexane	10.74	1.022	1.005
Heptane	12.28	1.028	1.000
Octane	13.82	1.031	0.995
Iso-pentane	7.56	0.996	1.005
Di-iso-propyl	7.56	0.998	1.007
Di-iso-butyl	10.74	1.016	0.999
Methyl formate	6.43	1.046	1.062
Ethyl ..	7.97	1.039	1.041
Propyl ..	9.51	1.032	1.022
Methyl acetate	7.42	1.051	1.057
Ethyl ..	8.96	1.053	1.046
Propyl ..	10.50	1.049	1.031
Methyl propionate	8.96	1.042	1.035
Ethyl ..	10.50	1.046	1.028
Methyl butyrate	10.50	1.041	1.023
.. iso-butyrate	8.96	1.031	1.025
Ethyl ether.....	8.96	1.017	1.012
Benzene	7.30	1.001	1.012
Fluorbenzene.....	7.90	1.012	1.017
Chlorbenzene	8.65	1.007	1.006
Brombenzene	8.93	1.016	1.012
Iodobenzene... ..	9.35	1.008	1.001
Methyl chloride.....	4.39	1.016	1.065
Carbon tetrachloride	5.74	0.981	1.010
Tin tetrachloride	7.00	0.997	1.011
Methyl alcohol	4.34	1.216	1.259
Ethyl ..	5.88	1.074	1.097
Propyl ..	7.42	1.066	1.072
Acetic acid	5.88	1.332	1.341
Acetonitrile	5.13	1.452	1.470
Propionitrile	6.67	1.306	1.305
Water	2.80	1.189	1.270
Ammonia	2.80	1.020	1.091
Hydrogen chloride	2.85	0.973	1.057

It is interesting to note that the expression

$$n_c = \frac{4}{15} \frac{RT_c}{P_c V_c},$$

uncorrected for the influence of the length of the molecule, indicates that the permanent gases are dissociated, whilst Guye's molecular refraction method indicates that they are associated. The method described in this paper indicates that they are normal substances, and this is probably the truth.

Summary.

It has been shown that the critical coefficient $\frac{RT_c}{P_c V_c}$ is a function of the length of the molecule in the case of the saturated paraffins and certain other normal substances. Making use of this relationship the association factors of forty-one substances at the critical point have been calculated. The values thus obtained are rational and in accordance with what might be expected from the general properties of these substances.

PART II.—THE INFLUENCE OF MOLECULAR ASSOCIATION ON THE CRITICAL CONSTANTS.

It has been shown in Part I. that the equation

$$\left(P + \frac{a}{(n_c V)^{5.3}}\right)(n_c V - b) = RT \times \frac{1}{f(l)} \quad \dots (3)$$

is very nearly accurate at the critical point. It would be possible, therefore, by means of this equation to calculate the influence of the association factor n_c on the critical constants, if its influence on the constants " a ," " b ," and " l " were known. The influence of molecular association on " l " has been discussed in Part I. If the molecular attractive power " a " and the molecular volume " b " were strictly additive quantities their values for double molecules would be $2a$ and $2b$. In actual fact they are nearly additive in non-associated homologous series, but " b " in particular shows marked irregularities in the case of very small molecules such as hydrogen and methane. Le Bas has discussed these irregularities*, which are equally noticeable in the

* G. le Bas, 'The Molecular Association of Liquid Chemical Compounds,' pp. 24 & 124, 1915 (Longmans, Green, & Co.). The author's views on this matter are rather complex.

molecular volumes at the boiling-point, and he appears to regard these divergences from the additive law as functions of the molecular volume. The present author finds that they can be represented as a function of the molecular length, and though the evidence at present available is insufficient to enable one to decide on the relative merits of these two views, the latter has been adopted for the sake of convenience. This correction is very small except in the case of small molecules, such as methane and hydrogen. This is illustrated by the values in Table I., where the correction factors calculated from the functions of " l " are tabulated. The correction for hydrogen is very nearly 250 per cent., that for methane is 22 per cent., and for the remainder it is small. The molecular attraction constant " a " is so nearly additive that very little alteration is needed, but such divergences as there are can be corrected for quite satisfactorily by an empirical function of " l ." Thus for " a " and " b " in equation (3), one may substitute the following expressions :—

$$a = \alpha \times [f(l)]^{2.3},$$

$$b = \beta \times f(l) \times f'(l),$$

where $f(l) = 0.838 + 0.174 \log l$ (as in equation (3))

and $f'(l) = 1 \times \frac{12.2}{l^3}$.

These expressions are constants for a given substance and do not therefore affect the validity of the equation, and since " α " and " β " are now very nearly additive it is possible to write 2α and 2β for double molecules. If the theory of mixtures were followed exactly very complicated expressions would ensue, but the errors introduced by writing $n \times \alpha$, $n \times \beta$, and $n \times l$ for an associated substance would be small; thus equation (1) becomes

$$\left(P + \frac{n^{1+x} \times \alpha \times [f(l)]^{2.3}}{(nV)} \right) (nV - n^{1+x+y} \times \beta \times f(l)(f'(l)))$$

$$= \frac{RT}{n^x \times f(l)}, \quad \dots \quad (5)$$

where V = volume of a gram formula weight,

n = association factor,

$$x = \frac{\log \frac{f(2l)}{f(l)}}{\log 2}, \quad y = \frac{\log \frac{f'(2l)}{f'(l)}}{\log 2},$$

in which the approximation for $f(nl)$, suggested in Part I., p. 115, is made use of.

Solving this equation for the critical point, we get

$$n_c^{1+\alpha} = \frac{4}{15} \frac{RT_c}{P_c V_c} \times \frac{1}{f(l)}, \quad \dots \quad (6)$$

$$\alpha = 4 \times \left(\frac{4}{15}\right)^{5.3} \times \frac{(RT_c)^{5.3}}{P_c^{2.3}} \times \frac{1}{n_c^{1+\alpha} [f(l)]^{1.3}}, \quad \dots \quad (7)$$

$$\beta = \frac{1}{15} \frac{RT_c}{P_c} \times \frac{1}{n_c^{1+2\alpha+y} [f(l)]^2 \times f''(l)}, \quad \dots \quad (8)$$

Values of α and β for various saturated paraffins are recorded in Table II. In calculating these values it has been assumed that " n_c " is equal to unity. Values of $\Sigma\alpha_a$ and $\Sigma\beta_a$ calculated by summation of the following atomic values,

	α_a	β_a
Hydrogen	0.30	.00235
Carbon	2.99	.00940

are recorded for comparison, and indicate that α and β are approximately additive so far as the saturated paraffins are concerned. Here it may be noted that Lø Bas has been followed in that a volume has been assigned to carbon which is equal to four times that of hydrogen. Less satisfactory results are obtained if a ratio of one to two is employed, the value for elementary hydrogen being particularly unsatisfactory and different from the value which it has in the hydrocarbons. The manner in which the functions of " l " (the values of which are also tabulated) contribute to the additive nature of α and β can be appreciated only after a careful study of Table II. For example, the values of α for

TABLE II.

	l	$[f(l)]^{1.3}$	α	$\Sigma\alpha_a$	$f'(l) \times [f(l)]^2$	β	$\Sigma\beta_a$
Hydrogen.....	1.5	.721	.55	.60	3.496	.0041	.0047
Methane	3.04	.827	4.09	4.19	1.219	.0187	.0188
Ethane	4.58	.894	7.93	7.78	1.024	.0333	.0329
Propane	6.12	.943	11.30	11.37	1.001	.0469	.0470
Butane	7.56	.979	14.96	14.96	1.011	.0612	.0611
Pentane	9.20	1.013	18.45	18.55	1.028	.0758	.0752
Hexane	10.74	1.041	22.28	22.14	1.046	.0898	.0893
Heptane	12.28	1.065	25.73	25.73	1.068	.1029	.1034
Octane	13.82	1.087	29.17	29.32	1.080	.1170	.1175
Iso-pentane	7.56	.979	18.76	18.55	1.011	.0758	.0752
Di-iso-propyl ...	7.56	.979	22.55	22.14	1.011	.0881	.0893
Di-iso-butyl	10.74	1.041	28.81	29.32	1.046	.1172	.1175

the isomers hexane and di-iso-propyl should be identical. They are 22.3 and 22.6 respectively, and thus differ by only one per cent. The values of the function of "*l*" differ by 6 per cent. Again, the values of β for the isomers octane and di-iso-butyl are practically identical, while the values of the corresponding functions of "*l*" differ by 3.5 per cent. In both these cases there would have been a divergence of several per cent. from the additive law but for the corrective influence of the functions of "*l*", which not only account satisfactorily for the influence of growing chains in normal saturated hydrocarbons, but also for certain isomeric rearrangements involving a change in the length of the molecule. The fact that β is additive for the early members of the paraffin series as well as for the later members has an important bearing on the question of molecular volumes, which will be dealt with at another time. It is not necessary for the present purpose that the values of α and β should be unchangeable for a given element and independent of environment. The fact that α_a for oxygen has a much smaller value in the esters than in the alcohols, and that α_a for hydrogen and carbon in the esters is slightly smaller than in the paraffins, is not a matter of great importance. All that is required is that atoms and groups shall retain their attractive power and volume unchanged so long as no serious change in chemical constitution is involved.

Values of α and β have been calculated for the various esters examined by Young, and these are recorded in Table III. Values of $\Sigma\alpha_a$ and $\Sigma\beta_a$ are recorded for comparison, and have been calculated from the following values:—

	α_a	β_a
Hydrogen	.26	.00231
Carbon	3.14	.00928
(—C—O—	6.52	.0231

The values of α_a found for carbon and hydrogen are smaller than the corresponding values for the paraffin hydrocarbons, but the values of β_a are practically the same. The general concordance between α and β and the corresponding quantities calculated by summation of the atomic and group values demonstrates their essentially additive nature. A

TABLE III.

	l .	n_c .	α .	$\Sigma\alpha_a$.	β .	$\Sigma\beta_a$.
Methyl formate	6.43	1.062	13.36	13.32	.0420	.0417
Ethyl "	7.97	1.041	16.55	16.46	.0561	.0556
Propyl "	9.51	1.022	19.98	19.60	.0695	.0695
Methyl acetate	7.42	1.057	16.49	16.46	.0558	.0556
Ethyl "	8.96	1.046	19.44	19.60	.0699	.0695
Propyl "	10.50	1.031	22.81	22.74	.0838	.0834
Methyl propionate	8.96	1.035	19.59	19.60	.0689	.0695
Ethyl "	10.50	1.028	22.65	22.74	.0836	.0834
Methyl butyrate	10.50	1.023	22.73	22.74	.0826	.0834
Methyl iso-butyrate	8.96	1.025	22.66	22.74	.0829	.0834

more searching proof of the validity of equation (5) for associated substances would be to show that α and β retain their additive character for series of highly associated substances, such as the alcohols and nitriles. Unfortunately, full data are available only for a few substances out of these two series. Table IV. shows that if the effect of association

TABLE IV.

	α' .	Δ for CH_2 .	β' .	Δ for CH_2 .
Methyl alcohol	14.0		.0346	
Ethyl "	15.4	1.4	.0448	.0102
Propyl "	18.4	3.0	.0581	.0133
Acetonitrile.....	20.7		.0618	
Propionitrile	22.1	1.4	.0742	.0124
Butyronitrile	23.2	1.1	.0838	.0096
Capronitrile	30.0	3.4×2	.0995	$.0078 \times 2$

is neglected, the value of " n_c " being taken as unity, the values of α' and β' thus obtained are far from being additive quantities, the differences for the homologous increment being abnormal and variable. When the association factors calculated in Part I. are employed these anomalies disappear. The true values of α and β cannot be calculated in the case of butyro- and capronitrile, since the critical volumes of these substances have not been measured, but the true values of the remaining five substances, together with those

TABLE V.

	<i>l</i> .	<i>n_c</i> .	<i>α</i> .	<i>Δ</i> for CH ₂ .	<i>β</i> .	<i>Δ</i> for CH ₂ .
Methyl alcohol	4.34	1.259	10.48		.0276	
Ethyl ,, ...	5.88	1.097	13.83	3.35	.0405	.0129
Propyl ,, ...	7.42	1.072	16.90	3.07	.0537	.0132
Acetonitrile	5.13	1.470	13.14		.0413	
Propionitrile	6.67	1.305	16.76	3.62	.0531	.0118
Acetic acid.....	5.88	1.341	14.69		.0415	

for acetic acid, are recorded in Table V. The anomalies remarked in Table IV. have disappeared. The differences for the homologous increment are more nearly normal, and in the case of the alcohols the values of these increments do not differ much from one another. The value of β for acetic acid is very nearly the same as that for the isomeric methyl formate. The value of α is higher than that for methyl formate, but this is not surprising, since it is found that hydroxyl oxygen has a greater attractive power than oxygen in any other form. A comparison of the values of α and β for ethyl ether with those for the alcohols yields similar results. α_a for etheric oxygen is much less than for hydroxyl oxygen, while β_a is practically the same in both cases. All these facts taken together give support to the view that equation (5) represents the relationship between the critical constants and the association factor with some approach to accuracy. It should be possible, therefore, by means of this equation to determine the influence of molecular association on the three critical constants.

Solving equation (5) for temperature, pressure, and volume at the critical point, we get

$$T_c = \frac{15}{4^{5/3} \times R} \times \frac{\alpha}{\beta^{2/3}} \times f(l) f'(l)^{-2/3} \times n_c^{1+x-1/2y}, \quad (9)$$

$$P_c = \frac{1}{4^{5/3}} \times \frac{\alpha}{\beta^{5/3}} \times f(l) f'(l)^{-5/3} \times n_c^{-1-x-5/2y}, \quad (10)$$

$$V_c = 4\beta \times f(l) f'(l) \times n_c^{x+y}. \quad (11)$$

From these three expressions the influence of the association factor on the critical constants can be determined. Unfortunately, the validity of these derived equations cannot be proved by direct observation, since up to the present no one has succeeded in determining the critical constants of a sub-

stance in any state of association other than that which is natural at the critical point, though Baker's experiments on very carefully dried substances indicate the possibility that this may be achieved eventually. It is possible, however, to compare the critical constants of pairs of substances such as benzene and diphenyl, and to see if these are in agreement with equations (9), (10), and (11). Diphenyl is slightly less than twice a benzene molecule, accordingly neither α nor β nor l is exactly doubled. Thus, for example, when two molecules of benzene are joined together with the elimination of two atoms of hydrogen to form a molecule of diphenyl, $\Sigma\alpha$ is increased 1.970 times, $\Sigma\beta$ is increased 1.933 times, and " l " is increased from 7.3 to 13.1 (*i. e.*, $2 \times [7.3 - 0.75]$). From these data one can calculate the effect of thus nearly doubling the size of the molecule on the critical constants of benzene on the assumption that n_c (which, in the case of hydrocarbons, differs but little from unity) remains constant, by means of equations (9), (10), and (11). The results of these calculations for the critical temperature and the critical pressure are given in Table VI.,

TABLE VI.

Substance.	Ratio of Critical Temperatures.	Ratio of Critical Pressures.
	$\frac{T_c \text{ double molecule}}{T_c \text{ single molecule}}$	$\frac{P_c \text{ double molecule}}{P_c \text{ single molecule}}$
$\text{H}_3\text{C}-\text{CH}_3$	1.55 (1.60)	1.06 (1.07)
$\text{H}_3\text{C}_2-\text{C}_2\text{H}_3$	1.41 (1.39)	0.766 (0.769)
$\text{H}_7\text{C}_3-\text{C}_3\text{H}_7$	1.37 (1.37)	0.686 (0.686)
$\text{H}_9\text{C}_4-\text{C}_4\text{H}_9$	1.33 (1.34)	0.656 (0.657)
	1.38 (1.37)	0.666 (0.663)
$\text{H}_2\text{C}:\text{H}_3\text{C}_2-\text{C}_2\text{H}_3:\text{CH}_2$	1.37 (1.37)	0.692 —
$\text{H}_2\text{C}:\text{H}_7\text{C}_4-\text{C}_4\text{H}_7:\text{CH}_2$	1.34 (1.30)	0.640 —

Observed values are printed in parentheses.

together with similar calculations for six other hydrocarbons, and the observed values for these substances calculated from

the actual critical data. From these values it is seen that the critical temperature is always increased by doubling the size of the molecule, and that the critical pressure, though usually reduced under these circumstances, is in the case of methane (a short molecule) actually increased. Reliable experimental data for checking the calculated critical volume ratios are not to be found in the literature; these are therefore omitted from the table. It may be stated, however, that they are in general agreement with the ratios calculated from the molecular volumes at the boiling-point. The calculated critical temperature and critical pressure ratios are in very good agreement with those found by experiment. It is therefore reasonable to conclude that equations (9), (10), and (11) are in accordance with the facts, and that it is possible by means of them to determine the influence of molecular association on the critical constants.

The question now arises as to the exact physical meaning of the constants α and β . Equation (5) has been derived from van der Waals's equation by means of empirical modifications introduced in order

- (a) to make the equation reasonably accurate at the critical point;
- (b) to make the constants additive in order that one might write $n\alpha$ and $n\beta$ for an associated substance.

One cannot, therefore, be sure that α and β represent accurately the molecular attractive power and the molecular volume respectively. There is much evidence, including that afforded by molecular refraction, to show that the space occupied by the molecules is additive with respect to the atoms and atomic groups of which the molecule is built up. It is, moreover, intrinsically probable that both the volume of the molecule and the molecular attractive power should be additive in the limited sense suggested in this paper. It therefore seems probable that α and β may be more closely proportional to the true values of the physical properties they claim to represent than " a " and " b " determined from the critical constants by the theoretically derived equation of van der Waals.

An absolutely independent method* of measuring the molecular attractive power of substances in solution was devised by H. E. Armstrong and the present author, and it was found that this quantity was approximately additive. This molecular attractive power was estimated from the

* Proc. Roy. Soc. A, lxxxix, p. 375 (1914).

effect of the substance on the rotatory power of fructose in aqueous solution by means of the expression

$$A = \frac{1}{M} (0.037 \Delta V - \Delta[\alpha]),$$

where A = molecular attractive power of solute,

M = molecular proportions of solute added,

ΔV = increase in volume produced by the addition of the solute,

$\Delta[\alpha]$ = change in rotatory power of the fructose in solution.

From this expression values of the molecular attractive power were calculated, and from these values atomic values were deduced. These are given below, together with the relative values of α_a :—

Atom or Group.	α_a .	$0.085 \alpha_a$.
—H	negligible	·026
>CH ₂	0.23	·267
—OH	0.70	·616
—C : N	0.74 *	·788

The parallelism between the two sets of values gives some support to the view that both A and α are measures of the molecular attractive power. It should be pointed out, however, that, for the purpose of the argument put forward in this paper, it is not absolutely necessary that α , β , and l should represent accurately the molecular attractive power, the molecular volume, and the molecular length. Equation (5) may be regarded as an empirical relationship between the critical constants containing the three quantities α , β , and l , which are found to be additive in the sense that they become approximately $n\alpha$, $n\beta$, and nl when the substance is associated n -fold.

Summary.

It has been shown that the constants α and β in a modified equation of state are additive quantities, both in the case of associated and unassociated substances. By means of this equation the effect on the critical constants of doubling the

* This is not the value given in the paper referred to, but it is that which is obtained if the same equation is used as that employed for the other two values. A less accurate expression was used in the paper, which neglected the influence of the homologous increment.

size of the molecule can be calculated, and the results of these calculations are in good agreement with existing experimental data. From this it is concluded that the modified equation of state is suitable for calculating the effect of molecular association on the critical constants.

In the next paper it will be shown how a knowledge of the manner in which the critical constants are affected by the degree of association can be used to calculate the association factor of liquids at various temperatures.

The author desires to thank Professor Lowry for his helpful criticism of these papers.

XI. *On the Effect of Aural Fatigue upon the Critical Frequency of Pulsation of Tones.* By MOLLIE WEINBERG, M.A., M.Sc., Research Student of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, and FRANK ALLEN, Ph D., F.R.S.C., Professor of Physics, University of Manitoba*.

THIS investigation is concerned with the effects of fatigue upon the persistence of audition, or the duration of the tone at the critical frequency of pulsation or flutter. The results herein described seem to throw new light upon some of the phenomena of acoustics, and also upon the probable structure of the aural mechanism by means of which tones are perceived and differentiated from each other.

The apparatus used is the same as that described in a previous communication†.

The source of sound was a tonvariator blown by a stream of air from a constant-pressure tank. The tonvariator was enclosed in a sound-proof box having one opening through which the sound could escape. The periodic interruption of the continuous sound was effected by the rotation of an aluminium disk in which were four holes of the same size as that of the opening in the box. For measuring the time of rotation of the disk, a speed counter and a clock beating half-seconds were electrically connected to a chronograph. When making measurements, the speed of the disk was adjusted so that the pulsation or flutter of the sound became just imperceptible, and then recorded. For fatiguing the

* Communicated by the Authors. Read at the meeting of the Royal Society of Canada, Ottawa, May 1922.

† "On the Critical Frequency of Pulsation of Tones," *supra*, p. 50.

ear, another tonvariator similar in all respects to the one in the sound-proof box, was used. Both instruments were calibrated from Standard Tuning Forks.

An attempt was made to determine the progressive effect of fatigue for increasing intervals of time, but the results were too uncertain to be of much use. The maximum fatigue seemed, however, to be attained in about two minutes for low intensities of sound. In the following experiments this interval of time was therefore allowed for fatiguing the ear before each measurement was made.

Two methods were used in this part of the work, one the converse of the other, in the hope that the results obtained from one would confirm those obtained from the other. Such happily appeared to be the case.

The first method consisted in fatiguing the ear with a tone of constant frequency, and taking measurements on tones varying over a range of about fifteen vibrations above and the same number below the fatiguing tone. The second method consisted in taking measurements on a tone of constant frequency, and varying the fatiguing stimulus over a similar range of about thirty vibrations.

In making measurements the following procedure was adopted. At a definite blowing-pressure, the tonvariator in the box, upon which the measurements were made, was adjusted to give a tone of any desired pitch, and the second tonvariator was accurately tuned with it by means of eliminating beats. The left ear was then fatigued with this tone for two minutes by holding it close to the orifice of the tonvariator, and immediately afterwards the measurement of the critical frequency of pulsation or flutter of tone was made. The fatiguing process was again and again repeated, and similar measurements were made on a selected series of tones.

Sets of such measurements are given in Table I. The persistency curves defined by these points were taken to represent the effect produced by fatiguing the ear with tones of constant frequency. The curves are shown in fig. 1. The curve through the small circles is the normal obtained with the unfatigued ear, and is plotted from the data in Table VI., F, which is taken from a former communication*. The broken line curves through the x's are the fatigue curves. These are characterized by prominent elevations covering in each case a range of about sixteen vibrations, with the maximum occurring at the frequency of the fatiguing tone, as is to be expected.

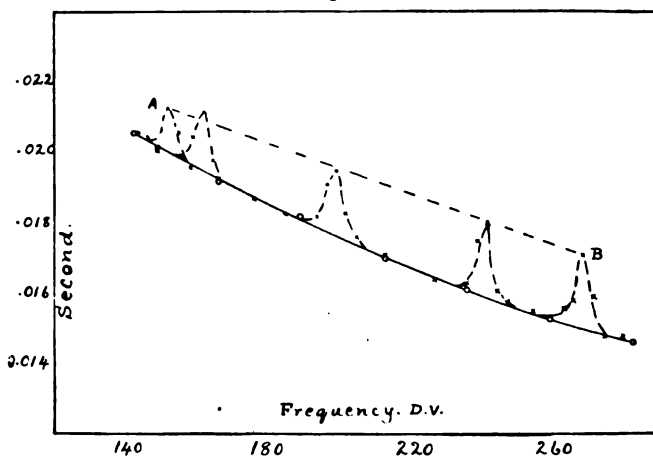
* "On the Critical Frequency of Pulsation of Tones," *supra*, p. 50.

TABLE I.

Fatigue Curves for different Frequencies at same Pressure.

Pressure.	Frequency.	Duration.	Pressure.	Frequency.	Duration.
P.	N.	D.	P.	N.	D.
Normal Curve.			Fatigue Curves (cont.).		
	D.V.	Sec.		D.V.	Sec.
1.82 cm.	143.0	0.0206	1.82 cm.	149.0	0.0201
"	167.0	.0192	"	156.4	.0199
"	190.0	.0187	"	159.2	.0205
"	214.0	.0170	"	162.2	.0212
"	237.0	.0161	"	165.0	.0198
"	260.5	.0153	"	168.0	.0192
"	284.0	.0146	"	176.5	.0187
Fatigue Curves.					
1.82 cm.	133.0	0.0206	1.82 cm.	185.8	0.0183
"	146.0	.0205	"	194.5	.0182
"	149.5	.0202	"	197.2	.0191
"	152.5	.0213	"	200.0	.0195
"	155.5	.0206	"	202.8	.0183
"	158.2	.0196	"	205.6	.0176
"	167.0	.0193	"	213.8	.0171
1.82 cm.	227.8	0.0164	1.82 cm.	255.8	0.0155
"	237.0	.0163	"	264.0	.0156
"	240.0	.0175	"	267.0	.0158
"	242.8	.0180	"	269.6	.0171
"	245.5	.0181	"	272.4	.0159
"	248.2	.0158	"	275.2	.0148
"	255.8	.0155	"	281.0	.0148

Fig. 1.



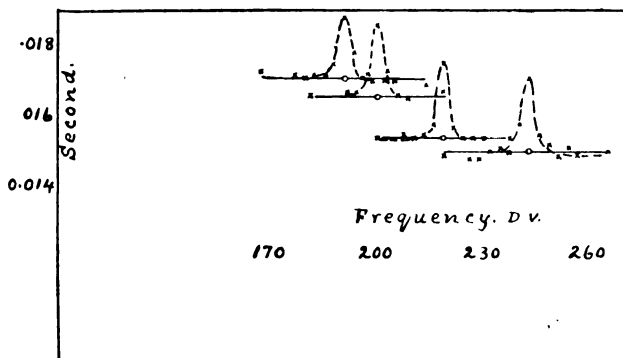
By the converse method, similar fatigue curves were obtained, the measurements being made, in each case, on a constant tone, and the fatiguing tone being varied over a range of about forty vibrations, as shown in Table II. These fatigue curves are plotted in fig. 2. The elevations in these

TABLE II.

Fatigue Curves—by Second Method (Constant Pressure).

P.	N'.	D. Sec.	P.	N'.	D. Sec.
	Normal Point.			Normal Point.	
1.78 cm.	190.5	0.0171	1.78 cm.	218.0	0.0154
	Fatigue Curve.			Fatigue Curve.	
1.78 cm.	167.0	0.0173	1.78 cm.	200.0	0.0154
"	176.6	.0172	"	207.1	.0155
"	179.3	.0171	"	210.0	.0154
"	182.0	.0172	"	212.7	.0155
"	185.0	.0172	"	215.7	.0158
"	187.5	.0175	"	218.4	.0175
"	190.5	.0188	"	221.3	.0157
"	193.2	.0178	"	224.0	.0154
"	196.0	.0171	"	226.6	.0154
"	198.5	.0170	"	229.8	.0154
"	201.7	.0170	"	237.1	.0154
"	204.5	.0170			
"	213.6	.0169			
	Normal Point.			Normal Point.	
1.78 cm.	199.8	0.0166	1.78 cm.	244.8	0.0150
	Fatigue Curve.			Fatigue Curve.	
1.78 cm.	181.0	0.0166	1.78 cm.	218.4	0.0149
"	191.2	.0167	"	226.0	.0148
"	194.0	.0167	"	228.7	.0148
"	196.9	.0172	"	231.6	.0150
"	199.8	.0186	"	234.5	.0151
"	202.6	.0173	"	237.0	.0150
"	205.3	.0166	"	240.0	.0157
"	208.1	.0165	"	242.8	.0171
"	218.4	.0167	"	245.5	.0155
			"	248.2	.0152
			"	251.0	.0149
			"	254.0	.0151
			"	256.8	.0149
			"	265.0	.0150

Fig. 2.



curves are symmetrical with the axis of frequencies, since the normal has only one value, which is the duration of the tone on which measurements were made at the critical frequency of pulsation. This is indicated in each case by a small circle at the proper frequency, through which the full horizontal line is drawn. The elevations again are found to cover the same range of about sixteen vibrations.

In the tables, P is the blowing pressure, in centimetres of water, to which the intensity of the sound of the tonvariator is proportional*; N is the frequency of vibration of the tonvariator; and D is the duration of the tone at the critical frequency of pulsation, or flutter.

The curves indicate that as a result of fatigue the persistency of sound impressions is greatly increased. This increase is a maximum when the frequency of the fatiguing tone is the same as that upon which measurements are taken, and diminishes very rapidly as the interval from the frequency of the fatiguing tone is increased. The entire range affected is about sixteen vibrations, or about eight on each side of the maximum. The steepness of the slope indicates that only a few vibrations very near the maximum on both sides are affected to any great extent.

The general nature of the fatigue curve is seen to be the same for each frequency. It will be noticed, especially in fig. 1, that as the frequency is increased the height of the elevation also increases. So perfectly do they vary together, that in this figure the maxima of the elevations lie on a straight line, shown in the figure as the broken line AB . No doubt if the ear were exposed to sounds of considerable intensity for a couple of minutes while instrumental adjustments were being made, the apparently "normal" curve thereby obtained would in reality be the straight line forming the locus of the maxima of the fatigue elevations. Possibly this may have been the case in Mayer's experiments, and may explain why his normal curves were straight lines, as indicated in a former communication†.

The elevations also show a slight gradual widening of their bases as the frequency is increased. This would indicate that the range of resonance arches in the ear affected by any tone is slightly greater as the frequency is raised. The range of frequencies used in this investigation, consisting of

* Misses Love and Dawson, *Phys. Rev.* vol. xiv. p. 49 (1919).

† "On the Critical Frequency of Pulsation of Tones," *supra*, p. 50.

but one octave, is, however, too small for any reliable conclusion to be drawn.

As indicated above, the elevations increase in height as the frequency of the fatiguing tone is increased. This may be caused by an increase in the sensitiveness of the resonating mechanism of the ear on account of pressure. In support of this idea an experiment due to Gelle may be cited. If a tuning-fork is pressed against the upper part of the forehead until its vibrations are faintly heard, and then a finger be pressed against the ear so as to increase the pressure on the membranes, the physiological intensity of the tone is greatly increased.

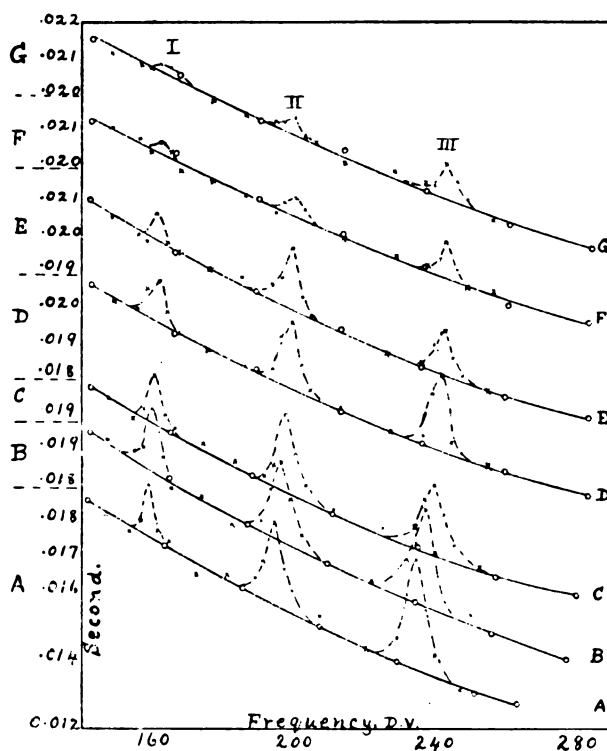
When the pitch of a tone is raised, the waves impinge upon the membranes of the ear with increasing frequency. The resonating arches may not therefore have sufficient time in which to recover from one impulse before the next wave arrives. The rising frequency of the tone may produce a certain steady increase of pressure, which, in turn, increases the sensitiveness of the auditory receptors. The resonating arches consequently are disproportionately fatigued and in such a condition respond more sluggishly to the stimulus, and the duration of the tone is increased when the frequency of pulsation reaches its critical value.

In fig. 3 are shown three (vertical) series of fatigue curves, each series representing the effect of fatigue of approximately the same frequency for seven different pressures or intensities. In series I. the fatiguing frequency was about 162, in series II. about 198, and in series III. about 240. The complete data are given in Table III. In examining this figure, it will be noticed that the lowest curve, A, is that for the lowest blowing-pressure, which gives the weakest tone, and the others represent tones gradually increasing in loudness. The curves are drawn to the same scale. The data for the normal curves are in Table VI. The columns N, in Table III., contain the tones upon which measurements were made.

The three series again show that the effect of fatigue is to increase the time of the critical frequency of pulsation. Also this increase becomes less as the intensity of the tone becomes greater. The diminutive size of the elevations in the curve G for the loudest tones employed indicates that for very intense sounds the fatigue elevations would disappear altogether. This might not be due, however, to the absence of fatigue, but to the probability that at higher intensities the ear is fatigued in much shorter time—that is, during the

time in which the measurements of the critical frequency of pulsation were being made. In that case, what would appear to be a smooth normal curve would in reality be the line through the maxima of a series of fatigue elevations as pointed out above. In fig. 3 the summits of the fatigue

Fig. 3.



elevations in the curves A, B, C, and D lie quite accurately on straight lines, and the remainder nearly so.

These curves are fully confirmed by others obtained by the second method—that is, by measuring the critical frequency of pulsation of a tone of constant frequency, the fatiguing tone being varied in pitch. The measurements are shown in Table IV, and the curves corresponding in fig. 4.

TABLE III.
Fatigue Curves. First Method.

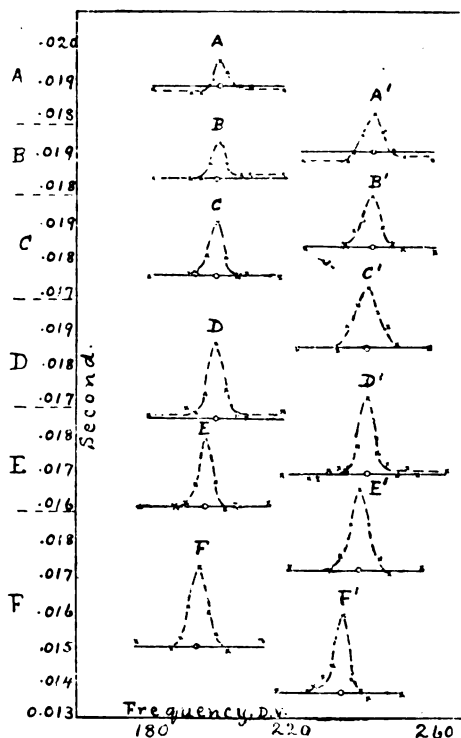
N.	D.	N.	D.	N.	D.
I G.		IIG.		IIIG.	
Press., 2.40 cm.		Press., 2.40 cm.		Press., 2.40 cm.	
Fatiguing Tone, 163.0.		Fatiguing Tone, 201.0.		Fatiguing Tone, 244.0.	
149.0	0.0211 sec.	186.7	0.0194 sec.	229.0	0.0178 sec.
157.2	0.0208	195.2	0.0193	238.4	0.0175
160.0	0.0207	198.0	0.0193	241.2	0.0174
163.0	0.0208	201.0	0.0193	244.0	0.0180
165.9	0.0207	203.8	0.0188	247.0	0.0175
168.0	0.0204	206.7	0.0186	249.8	0.0170
177.2	0.0198	215.0	0.0180	257.0	0.0164
I F.		II F.		IIIF.	
Press., 2.20 cm.		Press., 2.20 cm.		Press., 2.20 cm.	
Fatiguing Tone, 163.0.		Fatiguing Tone, 201.0.		Fatiguing Tone, 244.0.	
149.0	0.0210 sec.	186.7	0.0191 sec.	229.0	0.0174 sec.
157.2	0.0207	195.2	0.0186	238.4	0.0171
160.0	0.0203	198.0	0.0189	242.2	0.0173
163.0	0.0206	201.0	0.0190	244.0	0.0178
165.9	0.0203	203.8	0.0187	247.0	0.0170
168.8	0.0198	206.7	0.0183	249.8	0.0165
177.2	0.0195	215.0	0.0179	257.0	0.0164
I E.		II E.		IIIE.	
Press., 1.98 cm.		Press., 1.98 cm.		Press., 1.98 cm.	
Fatiguing Tone, 162.2.		Fatiguing Tone, 200.0.		Fatiguing Tone, 242.8.	
149.0	0.0205 sec.	185.8	0.0178 sec.	227.8	0.0167 sec.
156.4	0.0200	194.5	0.0176	237.0	0.0163
159.2	0.0198	197.2	0.0178	240.0	0.0169
162.2	0.0206	200.0	0.0186	242.8	0.0173
165.0	0.0198	202.8	0.0172	245.5	0.0165
168.0	0.0195	205.6	0.0167	248.2	0.0160
176.5	0.0190	213.8	0.0163	255.8	0.0156
I D.		II D.		IIID.	
Press., 1.82 cm.		Press., 1.82 cm.		Press., 1.82 cm.	
Fatiguing Tone, 162.2.		Fatiguing Tone, 200.0.		Fatiguing Tone, 242.8.	
149.0	0.0201 sec.	185.8	0.0183 sec.	227.8	0.0164 sec.
156.4	0.0199	194.5	0.0182	237.0	0.0163
159.2	0.0205	197.2	0.0191	240.0	0.0175
162.2	0.0207	200.0	0.0195	242.8	0.0180
165.0	0.0198	202.8	0.0183	245.5	0.0161
168.0	0.0192	205.6	0.0176	248.2	0.0158
176.5	0.0187	213.8	0.0171	255.8	0.0155
I C.		II C.		IIIC.	
Press., 1.53 cm.		Press., 1.53 cm.		Press., 1.53 cm.	
Fatiguing Tone, 161.0.		Fatiguing Tone, 198.0.		Fatiguing Tone, 240.3.	
147.5	0.0194 sec.	184.0	0.0176 sec.	225.8	0.0157 sec.
155.0	0.0188	192.3	0.0172	235.0	0.0157
158.0	0.0191	195.0	0.0175	237.6	0.0165
161.0	0.0200	198.0	0.0189	240.3	0.0169
163.9	0.0189	200.8	0.0178	243.0	0.0161
166.6	0.0185	203.5	0.0169	246.0	0.0152
175.0	0.0181	211.8	0.0162	253.0	0.0146

TABLE III. (*contd.*).
Fatigue Curves. First Method.

N.	D.	N.	D.	N.	D.
I B.		II B.		III B.	
Press., 1.45 cm.		Press., 1.45 cm.		Press., 1.45 cm.	
Fatiguing Tone, 160.8.		Fatiguing Tone, 197.0.		Fatiguing Tone, 238.0.	
147.3	0.0192 sec.	183.0	0.0168 sec.	222.8	0.0152 sec.
155.2	0.0189	191.2	0.0169	232.4	0.0158
158.0	0.0190	194.0	0.0178	235.2	0.0162
160.8	0.0201	197.0	0.0186	238.0	0.0172
163.6	0.0187	199.8	0.0175	240.8	0.0160
166.0	0.0178	202.5	0.0165	243.6	0.0146
174.3	0.0176	210.0	0.0158	251.0	0.0142

N.	D.	N.	D.	N.	D.
I A.		II A.		III A.	
Press., 1.25 cm.		Press., 1.25 cm.		Press., 1.25 cm.	
Fatiguing Tone, 159.4.		Fatiguing Tone, 195.0.		Fatiguing Tone, 235.2.	
147.0	0.0181 sec.	181.8	0.0164 sec.	221.2	0.0143 sec.
154.0	0.0176	189.6	0.0163	230.0	0.0146
156.9	0.0179	192.0	0.0168	232.7	0.0158
159.4	0.0189	195.0	0.0179	235.2	0.0168
162.0	0.0176	197.6	0.0165	238.0	0.0154
165.0	0.0173	200.0	0.0159	240.6	0.0141
173.0	0.0164	208.0	0.0152	247.8	0.0131

Fig. 4.



In Table IV. the tones in the columns, N', were the fatiguing tones.

TABLE IV.
Fatigue Curves. Second Method.

N'. A.	D. A.	N'. A'.	D. A'.	N'. D.	D. D.	N'. D.	D. D.
Press., 2.40 cm. Constant Tone, 201.0.		Press., 2.40 cm. Constant Tone, 244.0.		Press., 1.78 cm. Constant Tone, 199.8.		Press., 1.78 cm. Constant Tone, 242.8.	
182.0	0.0188	224.5	0.0168	181.0	0.0166	218.4	0.0149
192.5	0.0187	235.8	0.0168	191.2	0.0168	226.0	0.0148
195.2	0.0187	238.4	0.0170	194.0	0.0167	228.7	0.0148
198.0	0.0191	241.2	0.0175	196.9	0.0172	231.6	0.0150
201.0	0.0196	244.0	0.0181	199.8	0.0186	234.5	0.0151
203.8	0.0193	247.0	0.0176	202.6	0.0173	237.0	0.0151
206.7	0.0189	249.8	0.0171	205.3	0.0166	240.0	0.0157
209.5	0.0189	252.8	0.0169	208.1	0.0165	242.8	0.0171
219.0	0.0188	261.0	0.0168	218.4	0.0167	245.5	0.0155
						248.2	0.0152
						251.0	0.0149
						254.0	0.0151
						256.8	0.0149
						265.0	0.0150
B.		B'.		E.		E'.	
Press., 2.10 cm. Constant Tone, 201.0.		Press., 2.10 cm. Constant Tone, 244.0.		Press., 1.50 cm. Constant Tone, 197.0.		Press., 1.50 cm. Constant Tone, 240.3.	
182.0	0.0183	225.0	0.0163	178.0	0.0160	221.0	0.0143
192.5	0.0183	236.0	0.0164	188.2	0.0160	232.0	0.0142
195.2	0.0183	238.4	0.0168	191.2	0.0161	235.0	0.0146
198.0	0.0187	241.2	0.0171	194.0	0.0166	237.6	0.0155
201.0	0.0193	244.0	0.0178	197.0	0.0179	240.3	0.0165
203.0	0.0187	247.0	0.0169	199.8	0.0167	243.0	0.0155
206.7	0.0184	249.8	0.0164	202.5	0.0159	246.0	0.0145
209.5	0.0184	252.5	0.0163	205.2	0.0160	248.5	0.0141
219.0	0.0184	261.5	0.0162	215.0	0.0161	258.0	0.0143
C.		C'.		F.		F'.	
Press., 1.98 cm. Constant Tone, 200.0.		Press., 1.98 cm. Constant Tone, 242.8.		Press., 1.16 cm. Constant Tone, 195.0.		Press., 1.16 cm. Constant Tone, 235.2.	
181.0	0.0175	223.0	0.0155	177.0	0.0152	217.0	0.0138
191.8	0.0176	234.0	0.0154	187.0	0.0150	227.3	0.0139
194.5	0.0176	237.0	0.0161	189.6	0.0153	230.0	0.0142
197.2	0.0181	240.0	0.0167	192.0	0.0162	232.7	0.0145
200.0	0.0190	242.8	0.0172	195.0	0.0173	235.2	0.0159
202.8	0.0180	245.5	0.0165	197.6	0.0160	238.0	0.0141
205.6	0.0175	248.2	0.0161	200.0	0.0154	240.6	0.0138
208.4	0.0176	251.0	0.0156	203.0	0.0149	243.0	0.0136
218.0	0.0175	260.0	0.0155	212.3	0.0152	252.0	0.0137

As in the preceding figures, the height of the elevations shows that the persistence after fatigue becomes greater as the musical scale is ascended. The narrowness of the range of

frequencies affected is seen more clearly in this figure because the reference curve or normal upon which the fatigue elevation is superimposed is the continuous horizontal line drawn through the normal value of the critical frequency of pulsation which is marked with a small circle.

In fig. 4, also, are shown two series of fatigue curves, each for a nearly constant frequency, but varying blowing-pressures or intensities. The lowest curves in the figure are for tones of weakest intensity. Again, the decrease in the apparent effect of fatigue as the tone increases in intensity is clearly indicated, as is also the increase in the effect of fatigue with increase of frequency—*i. e.*, the height of A' is greater than that of A, of B' than B, etc. The two methods therefore give results that are perfectly consistent with each other.

These results of aural fatigue are susceptible of explanation by assuming the existence of a resonance mechanism in the ear. We may suppose that the organ of Corti is that mechanism, the forty-five hundred arches acting as a series of resonators. For the sake of brevity, let us term those arches possessing natural vibration frequencies corresponding exactly to that of an entering wave the resonal arches of that frequency, and two or three adjacent arches on each side of the resonals the auxiliary arches. The evidence from the curves may be interpreted as follows. When a train of simple waves enters the cochlea, the resonal arches are set into vibrations of corresponding amplitude. The auxiliary arches are also quite strongly affected. Further, the arches corresponding to about five or six additional vibrations on each side of the resonals are also rhythmically disturbed, but the amount to which they are affected very rapidly diminishes as their distance from the resonals increases. If the ordinates of the fatigue elevation may be considered to represent the relative amplitudes of the vibrating arches, the intensities of the tones from the resonals and the auxiliary arches will be very great compared with those from the more distant arches, which will thereby become negligible. The mainly effective vibrations may therefore be considered to be those of the resonal and auxiliary arches.

But since the natural periods of vibrations of the auxiliary arches differ from each other as well as from the resonals, it would apparently follow that a single train of waves would produce perceptible tones of about five different frequencies. In the octave under study, these tones would differ from each other in the extreme by about the interval of a comma, 81/80, which is near the usual limit of perceptible difference

in pitch. But the various arches vibrating in their natural periods would produce a series of beats which would be easily, as well as annoyingly, perceived.

This general objection, though urged by Watt * against the Helmholtz resonance theory, is removed by Helmholtz himself †. "An elastic body set into sympathetic vibrations by any tone vibrates sympathetically in the pitch number of the exciting tone; but as soon as the exciting tone ceases, it goes on sounding in the pitch number of its own proper tone. This fact, which is derived from theory, may be perfectly verified on tuning-forks by means of the vibration microscope."

This conclusion, applied to the present experimental results, indicates that the reason why the auxiliary arches are not heard in their natural frequencies is because they are constrained to vibrate with the same frequency as the resonals. As soon as the exciting tone ceases, the entire range affected also ceases to vibrate; the tones due to the natural frequencies of the auxiliaries are therefore not heard. The high degree of damping experienced by the vibrating arches immersed in the lymph of the cochlea quite naturally prevents any continuance of vibration after the exciting wave-train ceases to act.

The main objection of Watt to a resonance theory is that the arches on each side of the resonals do not give experiences in conformity with the law of specific energies of sense. Watt may have been justified in his criticism since, according to Helmholtz ‡ himself, the effect of an exciting tone was distinguishable on the resonating arches responding to a range of two whole-equally-tempered tones; that is, in the octave we are considering, about sixty-four vibrations. Helmholtz's curve is reproduced in fig. 5 in comparison with the fatigue curve of the tone of frequency 242.8, the measurements of the critical frequency of pulsation being made on a series of tones ranging from 218.4 to 265 vibrations, and the blowing-pressure being 1.78 cm. The data for the fatigue curve are given in Table V. The resonating arches disturbed, according to Helmholtz's curve, extend over a range more than four times as great as that indicated by the fatigue experiment. In estimating the data for his curve, Helmholtz states that exactness is out of the question. The method of the critical frequency of pulsation

* Watt, 'Psychology of Sound,' p. 142, 1917.

† Helmholtz, 'Sensations of Tone,' p. 144.

‡ *Loc. cit.*

combined with fatigue, however, enables measurements to be made with quite conclusive accuracy. The sharp-peaked character of the elevation of the fatigue curves, together with the very restricted range of frequencies disturbed, seem sufficient to remove from the resonance theory the objection urged by Watt.

Fig. 5.

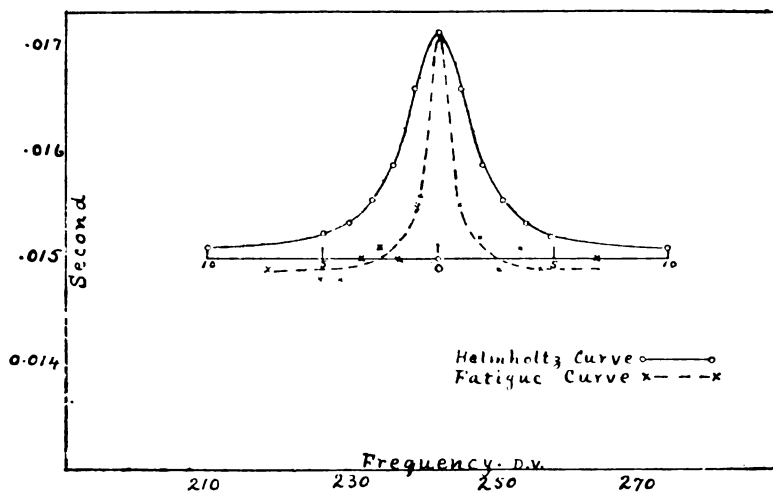


TABLE V.

Comparison of Helmholtz's Intensity Curve with Fatigue Curve.

P.	N'.	N.	D. Sec.
B. 1.78 cm.	218.4	242.8	0.0148
"	226.0	"	.0148
"	228.7	"	.0148
"	231.6	"	.0150
"	234.5	"	.0151
"	237.0	"	.0150
"	240.0	"	.0156
"	242.8	"	.0171
"	245.5	"	.0155
"	248.2	"	.0152
"	251.0	"	.0149
"	254.0	"	.0151
"	256.8	"	.0149
"	265.0	"	.0150

A. Helmholtz's Curve plotted from data in 'Sensations of Tone,' p. 144.

As pointed out above, the experiments herein described are limited to the octave from 142 to 284 vibrations. If the

character of the fatigue curves is the same in the octaves below as well as above, we can explain a well-known phenomenon in music.

It is universally recognized that shakes and runs in the bass are not clear, but that the tones merge into each other. This is independent of the instrument upon which they are played. Helmholtz * explains this as follows:—" Since the difficulty of shaking in the bass is the same for all instruments : and for individual instruments is demonstrably

TABLE VI.
Normal Curves.

Frequency. N.	Duration. D. Sec.	Pressure. P.	Frequency. N.	Duration. D. Sec.	Pressure. P.
A. 142.0	0.0185	1.25 cm.	F. 143.0	0.0206	1.82 cm.
164.0	.0172	"	167.0	.0192	"
186.0	.0160	"	190.0	.0182	"
208.0	.0149	"	214.0	.0170	"
230.0	.0139	"	237.0	.0161	"
252.0	.0130	"	260.5	.0153	"
264.0	.0127	"	284.0	.0146	"
B. 142.5	0.0194	1.45 cm.	G. 143.0	0.0210	1.98 cm.
165.5	.0181	"	167.0	.0195	"
187.5	.0168	"	190.0	.0184	"
210.0	.0157	"	214.0	.0173	"
235.0	.0146	"	237.0	.0163	"
256.7	.0137	"	260.5	.0154	"
278.0	.0130	"	284.0	.0148	"
C. 142.8	0.0197	1.53 cm.	H. 143.0	0.0211	2.10 cm.
165.8	.0184	"	167.2	.0200	"
188.8	.0172	"	190.2	.0187	"
211.8	.0161	"	214.2	.0177	"
235.7	.0152	"	237.2	.0166	"
257.9	.0143	"	260.7	.0158	"
280.5	.0138	"	284.2	.0151	"
D. 142.9	0.0201	1.62 cm.	I. 143.2	0.0212	2.20 cm.
166.2	.0187	"	167.3	.0203	"
189.0	.0177	"	191.0	.0190	"
212.0	.0166	"	214.6	.0180	"
235.3	.0155	"	238.0	.0171	"
258.2	.0146	"	261.2	.0160	"
280.9	.0140	"	284.2	.0155	"
E. 143.0	0.0203	1.70 cm.	J. 143.5	0.0215	2.40 cm.
166.6	.0190	"	168.2	.0205	"
189.7	.0179	"	191.2	.0192	"
213.2	.0168	"	215.0	.0184	"
236.2	.0158	"	238.3	.0173	"
259.3	.0149	"	261.9	.0163	"
283.0	.0143	"	285.0	.0156	"

* 'Sensations of Tone,' p. 143.

independent of the manner in which the tones are produced, we are forced to conclude that the difficulty lies in the ear itself. We have, then, a plain indication that the vibrating parts of the ear are not damped with sufficient force and rapidity to allow of successfully effecting such a rapid alternation of tones."

According to the experimental evidence of the fatigue curves, the blurring or merging together of tones in the bass is not due to the peculiar construction of the ear, nor to insufficient damping of the resonance mechanism, but is the natural consequence of the fact that the tones of the scale are not separated by absolute numbers of vibrations, but by numbers determined by fixed ratios.

The difference in vibration frequency between two successive tones in the treble is very large when compared with the difference between two such tones in the bass; for example, the difference between c'' , 512, and d'' , 576, is 64 vibrations, whereas the difference between C_1 , 32, and D_1 , 36, is only 4 vibrations. In a run in the treble, therefore, each tone is so far moved from the one preceding that the arches stimulated by the first tone are altogether outside the region of influence of the second. It can very clearly be seen therefore that, when c'' , d'' , e'' , f'' , etc. are sounded in rapid succession, the effect will be distinct and brilliant. And the higher the pitch of notes with which the runs and trills are made, the more distinct will each tone be from the other, and the more brilliant the total impression.

In the bass, on the other hand, the opposite will be the case. The difference between two successive tones is comparatively very small. As previously noted, the difference between C_1 and D_1 is only 4 vibrations, while an octave higher it is only 8 vibrations. Since the difference in frequency between consecutive tones is so small, many of the arches responding to one tone will also respond to the other; in fact, nearly the same range will be influenced by each tone. The arches most strongly affected will be the resonals of each tone, and these are themselves not far distant from each other. In fig. 1, in which fatigue curves for five frequencies at the same pressure are shown, it will be noticed that the elevations for 152 and 163 overlap to some extent. The difference in frequency in this instance is eleven vibrations. If the difference in frequency were smaller, the overlapping would be greater; therefore the farther down in the bass one attempts to produce a rapid succession or alternation of tones, the more nearly will the same range of resonators be influenced by adjacent tones, and the more indistinct and

blurred will be the general impression. If semitones are employed instead of tones, the indistinctness will be proportionately increased.

The results of this investigation seem to find their natural explanation in terms of the resonance theory of audition, and therefore no present attempt has been made to interpret them in accordance with the Wrightson displacement theory.

This research was conducted under the auspices of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, to which body we wish to express our thanks.

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XII. *On the Effect of Fatiguing the Ear with Combinations of Two or more Tones.* By MOLLIE WEINBERG, M.A., M.Sc., University of Manitoba, Winnipeg, Research Student in Physics of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa*.

IN this communication, the method of studying the effects of aural fatigue by the critical frequency of pulsation or flutter of tones is applied to fatigue with two and three tones simultaneously.

The experimental arrangements were the same as described in previous communications †, except in one particular. In the former work, the source of continuous sound—a Stern Tonvariator—was enclosed in a large wooden box lined with thick felt. The box, however, transmitted some of the sound, so that the rotating disk did not completely produce the ideal alternations of sound and silence. In these experiments the upper part of the tonvariator was enclosed in a box made of pressed fibre, which is an extremely poor transmitter of sound. Watson ‡ found that a plate of this material, one-quarter of an inch in thickness, was capable of transmitting only one-tenth of one per cent. of the sound. Accordingly, a box of suitable size and shape was constructed of the fibre,

* Communicated by Prof. F. Allen, M.A., Ph.D. Read at the meeting of the Royal Society of Canada, Ottawa, May 1923.

† "On the Critical Frequency of Pulsation of Tones," *supra*, p. 50.

‡ Physical Review, vol. vii. p. 125 (1916).

in one side of which a circular hole was cut, through which the continuous stream of sound issued. Periodical interruption of the sound-ray was effected by a rotating disk in which were four symmetrically placed holes similar to that in the box. This arrangement gave sharp and clear flutterings of the tone, and, in consequence, the speed of the disk could be accurately and rapidly adjusted to the critical frequency of flutter, so that the pulsations of sound appeared just continuous. Unfortunately, the dimensions of the box interfered to some extent with the range of frequencies that could be studied, and consequently only part of one octave of tones could be employed. For the investigations described in this communication, however, it served the purpose extremely well.

I. *Application of the Critical Frequency of Pulsation of Tones to Tone Analysis.*

In a former paper * it was found that, when the ear was fatigued by exposure to any tone, the duration of the tone at the critical frequency of flutter or pulsation was increased over a range of about eight vibrations on each side of the frequency of the fatiguing tone. When similar measurements were made with the ear in its normal unfatigued condition, and the two plotted together, the fatigue curve appeared as a sharp elevation upon the normal, the peak of the elevation occurring at the frequency of the fatiguing tone.

In the experiments herein described, two or three additional tonvariators were used to give simultaneous fatigue with two or three tones of determined frequencies. Suitable calibrations of these instruments were made so that the exact frequencies were determined.

The arrangement of apparatus is shown in fig. 1, in which A indicates the air current, G the pressure gauge, T the tonvariator, D the disk, E the ear, and S the speed counter.

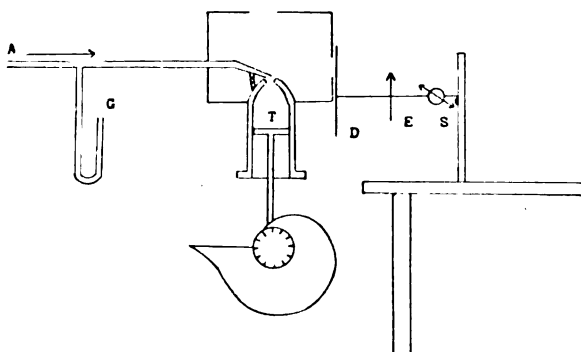
The method of procedure was as follows:—

At a definite blowing-pressure the tonvariator upon which measurements were to be made was adjusted to give a tone of definite pitch. The tonvariators used for the purpose of fatigue were then accurately tuned with it by eliminating beats, after which they were adjusted to give tones of desired frequencies. The left ear was then fatigued with these tones for two minutes by holding it close to the orifices of the

* "On the Effects of Aural Fatigue upon the Critical Frequency of Pulsation of Tones," *supra*, p. 126.

tonvariators. Immediately afterwards the measurement of the critical frequency of pulsation, or flutter, of a tone within the fatigued range of frequencies was made. The fatiguing process was again and again repeated, and similar measurements made at close intervals, over a range of frequencies including, and wider than, the range defined by the outermost fatiguing tones.

Fig. 1.



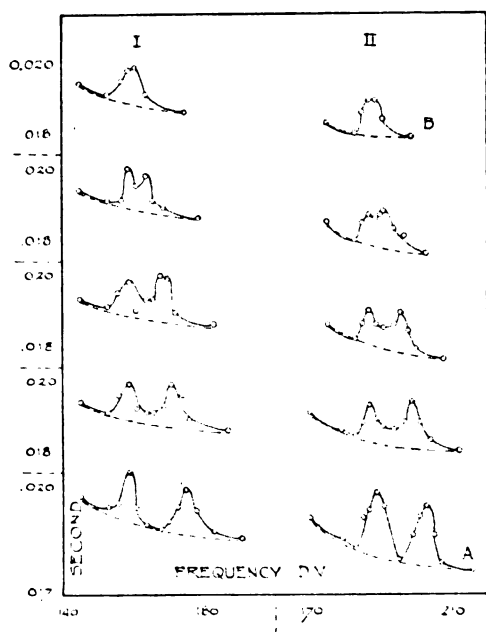
The first measurements were made with two fatiguing tones. These are tabulated in Table I., and the curves defined by them are shown in fig. 2.

The curve through the points not included in the elevation was taken to define the normal upon which the elevation is superimposed. This is indicated by the broken line. The elevation itself is similar to those obtained by fatiguing the ear with a single tone. The range affected by fatiguing, as shown by the width of the base of the elevation, is also approximately the same. In curve A the fatiguing tones were fifteen vibrations apart. Similar curves were obtained with fatiguing tones the frequencies of which, as shown in the table of values, slowly approached each other. Series I. in fig. 2 is such a set of curves. In this series the highest curve, B, was obtained with fatiguing tones that differed by two vibrations only, and curve A with tones that differed by fifteen vibrations; the intermediate curves were obtained with fatiguing tones which varied between these limits.

As can be seen from curve A, fig. 2, when the fatiguing tones are fifteen vibrations apart, there was very little overlapping in the elevations. Had they been about twenty vibrations apart, it is quite certain that each elevation would

be complete and distinct from the other, one elevation beginning at the point in the normal where the other ended. Interpreted according to the resonance theory of audition, this would seem to indicate that each of the fatiguing tones would affect a different set of arches—or whatever part of the resonating mechanism responds,—which, however, were adjacent to each other. From this it may be assumed that were the differences in frequency of the fatiguing tones greater than those used for these curves, the nature of the elevations would be the same, but with an increased extent

Fig. 2.



of normal curve between them—*i. e.*, the sets of arches influenced by the simultaneously fatiguing tones would be no longer adjacent, but would have a stretch of uninfluenced arches between them.

It can be seen from fig. 2, Series I., that, as the fatiguing tones approach each other, overlapping of the elevations takes place—*i. e.*, the curve between the maxima of the elevations no longer drops to the normal, but becomes more and more shallow until, when the difference in frequency is two vibrations, it has become a short, straight,

TABLE I.

Fatiguing with Two Tones simultaneously.

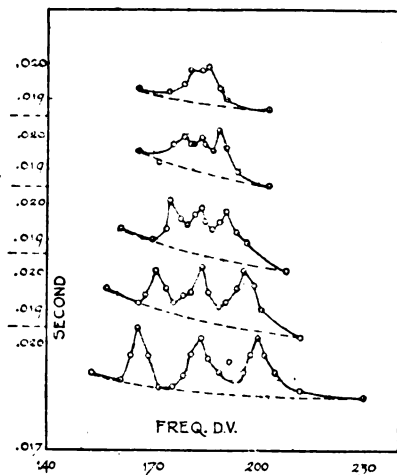
N.	D.	P.	N.	D.	P.	N.	D.	P.
I. Fatiguing Tones, 159 and 175.			I. Fatiguing Tones, 159 and 164.			II. Fatiguing Tones, 187 and 199 (<i>cont.</i>).		
D.V.	Sec.	Cm.	D.V.	Sec.	Cm.	D.V.	Sec.	Cm.
145	0.0198	1.60	145	0.0195	1.65	189	0.0190	1.55
153	0.0195	"	153	0.0192	"	191	0.0188	"
156	0.0196	"	157	0.0192	"	194	0.0187	"
159	0.0205	"	159	0.0201	"	197	0.0189	"
161	0.0195	"	161	0.0196	"	199	0.0195	"
164	0.0190	"	164	0.0199	"	201	0.0189	"
168	0.0189	"	166	0.0192	"	204	0.0184	"
170	0.0191	"	169	0.0190	"	212	0.0181	"
173	0.0195	"	179	0.0187	"			
175	0.0200	"				Fatiguing Tones, 187 and 196.		
178	0.0194	"	Fatiguing Tones, 159 and 161.			D.V.	Sec.	Cm.
183	0.0188	"	D.V.	Sec.	Cm.	175	0.0187	1.55
191	0.0186	"	145	0.0195	1.65	183	0.0183	"
			153	0.0192	"	185	0.0187	"
Fatiguing Tones, 159 and 171.			157	0.0196	"	187	0.0191	"
D.V.	Sec.	Cm.	159	0.0199	"	189	0.0187	"
145	0.0195	1.60	161	0.0200	"	191	0.0186	"
153	0.0192	"	164	0.0192	"	194	0.0187	"
156	0.0197	"	175	0.0187	"	196	0.0190	"
159	0.0200	"				198	0.0185	"
161	0.0193	"	II. Fatiguing Tones, 187 and 203.			200	0.0180	"
164	0.0192	"	D.V.	Sec.	Cm.	208	0.0177	"
166	0.0192	"	170	0.0192	1.55	Fatiguing Tones, 187 and 191.		
169	0.0194	"	179	0.0186	"	D.V.	Sec.	Cm.
171	0.0200	"	183	0.0183	"	175	0.0186	1.55
174	0.0197	"	185	0.0192	"	183	0.0181	"
176	0.0190	"	187	0.0194	"	185	0.0186	"
187	0.0187	"	189	0.0189	"	187	0.0188	"
			191	0.0185	"	189	0.0187	"
Fatiguing Tones, 159 and 168.			195	0.0180	"	190	0.0188	"
D.V.	Sec.	Cm.	199	0.0187	"	191	0.0189	"
145	0.0194	1.60	201	0.0192	"	194	0.0184	"
153	0.0192	"	203	0.0195	"	197	0.0182	"
156	0.0196	"	205	0.0187	"	203	0.0177	"
159	0.0199	"	207	0.0179	"			
161	0.0191	"	216	0.0177	"	Fatiguing Tones, 187 and 189.		
164	0.0194	"	Fatiguing Tones, 187 and 199.			D.V.	Sec.	Cm.
166	0.0194	"	D.V.	Sec.	Cm.	175	0.0184	1.55
168	0.0201	"	170	0.0192	1.55	183	0.0181	"
170	0.0200	"	179	0.0187	"	185	0.0187	"
172	0.0190	"	183	0.0185	"	187	0.0190	"
183	0.0187	"	185	0.0189	"	189	0.0190	"
			187	0.0194	"	191	0.0185	"
						199	0.0180	"

horizontal line. In other words, as the fatiguing tones approach each other, more and more of the arches responding to the one tone will simultaneously be under the influence of the other fatiguing tone until, when the fatiguing tones are very close together, approximately the same range is influenced by each.

Fig. 2, Series II., is a set of curves obtained in a similar manner to Series I., which shows the same effects over a range of frequencies higher up in the octave. It serves, therefore, as a confirming experiment. The data are also given in Table I., in which N is the frequency, D the duration of the tone at the critical frequency of flutter, and P is the pressure to which the intensity is proportional.

The above sets of curves seem explainable by no other than a resonance theory. The evidence afforded by them may therefore be taken as strongly supporting the theory, that

Fig. 3.



some resonating mechanism by means of which complex tones may be analysed into their components exists in the ear.

A series of experiments similar to those above described was then carried out, in which three simultaneously fatiguing tones were used. This series of curves is shown in fig. 3, and was plotted from data in Table II. The three-elevation curves exhibit the same peculiar characteristics as do the previously described two-elevation curves. Here, again, when the fatiguing tones are about sixteen vibrations apart,

TABLE II.

Fatiguing with Three Tones simultaneously.

N. D. P.			N. D. P.		
Fatiguing Tones, 166, 184, and 200.			Fatiguing Tones, 175, 184, and 191.		
D.V.	Sec.	Cm.	D.V.	Sec.	Cm.
153	0.0192	1.60	161	0.0193	1.50
161	0.0190	"	170	0.0190	"
164	0.0197	"	173	0.0194	"
166	0.0205	"	175	0.0201	"
169	0.0197	"	178	0.0196	"
172	0.0188	"	180	0.0194	"
176	0.0188	"	182	0.0197	"
179	0.0191	"	184	0.0199	"
181	0.0197	"	185	0.0195	"
184	0.0202	"	187	0.0193	"
186	0.0196	"	189	0.0195	"
189	0.0192	"	191	0.0198	"
192	0.0195	"	194	0.0192	"
196	0.0192	"	197	0.0189	"
198	0.0197	"	208	0.0181	"
200	0.0202	"			
203	0.0197	"	Fatiguing Tones, 179, 184, and 189.		
205	0.0192	"	D.V.	Sec.	Cm.
212	0.0187	"	166	0.0195	1.51
230	0.0185	"	172	0.0192	"
			176	0.0197	"
			179	0.0199	"
Fatiguing Tones, 171, 184, and 196.			181	0.0197	"
D.V.	Sec.	Cm.	182	0.0197	"
157	0.0196	1.57	184	0.0199	"
166	0.0192	"	185	0.0197	"
168	0.0184	"	187	0.0195	"
171	0.0201	"	189	0.0201	"
174	0.0196	"	191	0.0196	"
176	0.0192	"	194	0.0189	"
179	0.0194	"	203	0.0185	"
181	0.0195	"			
184	0.0202	"	Fatiguing Tones, 181, 184, and 186.		
186	0.0195	"	D.V.	Sec.	Cm.
189	0.0194	"	166	0.0193	1.50
191	0.0192	"	175	0.0192	"
194	0.0196	"	179	0.0194	"
196	0.0201	"	181	0.0198	"
199	0.0197	"	184	0.0198	"
201	0.0190	"	186	0.0199	"
212	0.0182	"	189	0.0193	"
			191	0.0190	"
			203	0.0187	"

each elevation slopes down almost, if not quite, to the normal. As the differences between the frequencies of the fatiguing tones are decreased, the curves between the peaks of the elevations again recede from the normal until, when they have approached each other very closely, there is a short, straight, horizontal line between them. At that point approximately the same range of arches is influenced by each

fatiguing tone, and the resonals of each—*i. e.*, those arches possessing natural vibration frequencies corresponding exactly with those of the entering tones—are adjacent to each other. In all cases, whether fatiguing with two or with three tones, the maxima of the elevations define the resonals.

The curves indicating the effects of fatigue caused by three tones are thus seen to be exactly similar in character to those for two tones. It may therefore be justifiably assumed that were the ear to be fatigued with more than three tones simultaneously, by a method of procedure similar to the one above described, a set of curves would be obtained possessing peculiarities similar to those possessed by the curves in figures 2 and 3; in all cases the highest peaks of the elevations would define the resonals—*i. e.*, the resonating arches corresponding to the frequencies of the fatiguing tones.

The above therefore indicates an altogether new and very interesting method of tone analysis. To analyse a compound tone would only necessitate repeated fatiguing with the given mixture of tones, each fatiguing process being accompanied by a corresponding persistency measurement; the entire procedure being extended over a range of frequencies within which, it is judged, the component tones lie.

II. *An Experimental Study of Differential Tones.*

Combinational tones are heard when two musical tones of different pitches are sounded together loudly and continuously. They are of two kinds—differential and summational tones. The pitch number of the differential is equal to the difference of the frequencies of the generating tones; and that of the summational tone is equal to the sum of the frequencies of the generating tones.

There are different orders of combinational tones. The differential, or combinational tone of the first order, is one of pitch equal to the difference of the vibration frequencies of the generating tones themselves. Combinational tones of the second order are formed by the combination of the generating tones with differentials of the first order. These again produce new combinational tones with other differentials. There are thus differential tones of many orders, the first-order differential being the loudest, the intensity decreasing rapidly as the order of the differential becomes higher.

This investigation deals with differential tones of the first order only.

The successful results obtained in investigating the effects of aural fatigue suggested the application of that method to determine the probable nature of the combinational tone.

The apparatus used was the same as that employed in the investigation in the first section of this paper.

The method of procedure was as follows:—

Two tonvariators were adjusted to give tones of such frequencies that their differential of the first order fell somewhere within the range of frequencies upon which measurements of the critical frequency of pulsation could be made. The true frequency of the differential tone was obtained from the calibration curves of the tonvariators made by comparison with tuning-forks. Fatiguing with the two generating tones simultaneously, and proceeding in a manner similar to that described in the previous section, measurements of the critical frequency of pulsation were made at very short intervals over a sufficiently wide range of frequencies which included the differential tone of the first order.

The resulting curves, plotted from the data in Table III.,

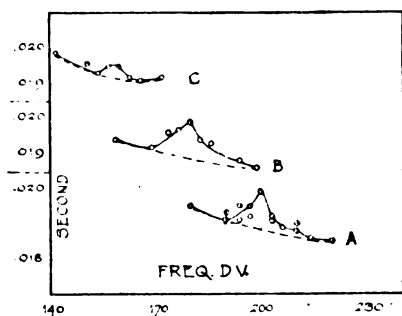
TABLE III.

Differential Tones of the First Order.

N.	D.	P.	N.	D.	P.
A. Generating Tones, 170 and 370.			B. Generating Tones, 220 and 400.		
Differential Tone, 200.			Differential Tone, 180.		
D.V.	Sec.	Cm.	D.V.	Sec.	Cm.
180	0·0195	1·55	159	0·0194	1·50
190	·0191	..	169	·0192	..
194	·0195	..	174	·0196	..
197	·0195	..	177	·0197	..
200	·0199	..	180	·0199	..
203	·0191	..	183	·0194	..
206	·0189	..	186	·0193	..
210	·0190	..	194	·0188	..
214	·0186	..	199	·0186	..
220	·0185	..			
Generating Tones, 150 and 350.			C. Generating Tones, 220 and 380.		
Differential Tone, 200.			Differential Tone, 160.		
D.V.	Sec.	Cm.	D.V.	Sec.	Cm.
180	0·0195	1·55	142	0·0199	1·45
190	·0193	..	151	·0196	..
194	·0191	..	154	·0193	..
197	·0192	..	157	·0195	..
200	·0199	..	160	·0195	..
203	·0192	..	163	·0192	..
206	·0189	..	166	·0191	..
210	·0188	..	172	·0192	..
220	·0185	..	182	·0191	..

are given in fig. 4. Each graph is seen to be a portion of a normal curve, broken by a short elevation similar to that obtained by direct fatigue. The peak of the elevation is at a frequency which very closely approximates that of the differential. Curve A is the average curve drawn through two sets of measurements, both for the differential tone of frequency 200, the generating tones of each set differing by that number. The frequencies of the generating tones are given in the table. This indicates that no matter what the generating tones may be, the combinational tone will influence the same portion of the resonating system if the difference of their vibration frequencies is the same.

Fig. 4.



Curves B and C were obtained in a similar manner to A, but for differing pitches of the differential. The characteristics of all the curves appear to be the same. Curve C is a little shallower than A and B.

The position of the maximum height of the elevations represents approximately the pitch of the differentials. The vertical heights of these elevations, however, are not as great as those representing fatigue caused by ordinary tones. This difference is probably due to the comparatively low intensity of the differential tones.

The graphs discussed may, with the aid of the resonance theory of audition, be interpreted in such a manner as to explain the probable nature of the differential tone. The elevations indicate that the differentials have as direct an effect upon portions of the series of resonating arches as have tones generated in the ordinary manner—*i. e.*, differential tones are objective in character.

It was formerly believed that combinational tones were subjective effects—*i. e.*, purely psychological phenomena.

Helmholtz * himself stated that there were both objective and subjective combinational tones. Preyer † carried out a series of experiments which seemed to prove the subjectivity of differential tones. The experimental evidence as given above, however, supports the theory that differential tones of the first order are objective, since they possess the same peculiarities of stimulation as do tones produced in the ordinary manner. In other words, they are physiological and not psychological in their origin.

It was hoped to carry through a series of experiments similar to those above described for summational tones. Since this would necessitate the taking of measurements over a range of frequencies far higher than that which could be measured with the experimental arrangements at the time, their study had to be postponed until the apparatus could be improved to allow measurements to be taken over a more extended range of frequencies.

Many attempts were therefore made to adapt the apparatus to higher octaves. But with frequencies above 300 d.v. the rotating disk was incapable of giving sufficiently marked alternations of intensity of the sound to be of any value. A new method of interruption of the sound-ray was found, but it has not yet been sufficiently developed to give reliable measurements.

In conclusion, it may be stated that the results of this investigation support the theory formulated by Helmholtz, that tones are perceived and differentiated from each other by means of a resonance mechanism which exists in the internal ear. From this general statement it is also clear that differential tones and probably summational tones are not excluded.

I wish to acknowledge my indebtedness to the kindness and valuable advice of Dr. Frank Allen, Director of the Department of Physics of the University of Manitoba, at whose suggestion and under whose direction the investigations here described were carried out.

I also desire to express my thanks to the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, under whose auspices this investigation was conducted.

Department of Physics,
University of Manitoba,
Winnipeg, Manitoba.

* Helmholtz, 'Sensations of Tone,' p. 531.

† *Loc. cit.* p. 531.

XIII. *On a Supposed Limitation of the Second Law of Thermodynamics.* By ENOS E. WITMER, Ph.D., *Harrison Research Fellow at the University of Pennsylvania* *.

IN an article in the *Phil. Mag.* (6) vol. xliii. p. 1047 (1922) Fairbourne gives a proof that if a vessel of suitable shape, typically a truncated cone open at both ends, be immersed in a gas so rarefied that the mean free path of the molecules is large compared with the dimensions of the vessel, the molecules entering in haphazard directions will be diverted to leave in one preponderating direction. This state of affairs would be contrary to the second law of thermodynamics, assuming its applicability in this case, since a paddle-wheel properly placed with respect to the vessel would yield mechanical work at the expense of the thermal energy of the gas. To many physicists the conclusion suggested that the argument was fallacious. The fallacy exists, and is pointed out below, I believe, for the first time.

Fairbourne's proof, for the details of which reference must be made to the original article, is based upon the following assumptions, expressed or implied :—

1. That the mean free path of the molecules of the gas surrounding the vessel is so great that intermolecular collisions in the vessel are occurring with only a negligibly small fraction of the total number of molecules which pass through in a representative period of time.

2. That regular reflexion of the molecules takes place at the sides of the vessel.

3. That there are no forces of attraction or repulsion between the sides of the vessel and the gas molecules.

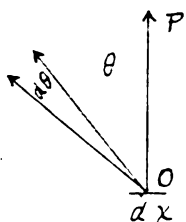
4. In the course of the argument, which is carried out in two dimensions, he explicitly makes the apparently justifiable assumption that at any point *O* in the face of the vessel "molecules will enter equally in all directions throughout 180° ."

The first three assumptions are admissible; the last one properly interpreted is also, but as it is applied in Fairbourne's proof, and as one would naturally interpret it, it is not admissible. The term "point" in this assumption is misleading. As is frequently the case in physics, the word "point" is used in Fairbourne's proof to signify not a point, strictly speaking, but an element of length. Put into rigorous terms, the last assumption, naturally interpreted, is that

* Communicated by Professor Bazzoni.

through the elementary length dx at the point O, molecules will enter equally in all directions throughout 180° . This statement is manifestly untrue.

Fig. 1.



Let dx be an element of length, OP the normal directed toward one side, and θ the angle between any direction and OP. Then if dn is the number of molecules crossing dx in directions included between θ and $\theta + d\theta$ in a time dt ,

$$dn = N \cos \theta \, dx \, d\theta \, dt, \quad \dots (1)$$

where N is a constant.

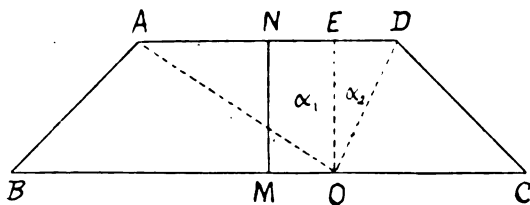
The false assumption discussed in the last paragraph is equivalent to the omission of the factor $\cos \theta$ in (1).

The number of molecules dn_1 which cross dx in directions included between $\theta=0$ and $\theta=\alpha$ is

$$\begin{aligned} dn_1 &= N \, dx \, dt \int_0^\alpha \cos \theta \, d\theta \\ &= N \sin \alpha \, dx \, dt. \quad \dots (2) \end{aligned}$$

We shall now carry through the reasoning with the modification indicated for the first vessel considered by Fairbourn, and show that the same number of molecules pass through the vessel upwards as downwards.

Fig. 2.



The two-dimensional vessel is ABCD (fig. 2). AB and CD are the sides, while AD and BC are open.

$$\angle ABC = \angle BCD = 45^\circ,$$

AD is parallel to BC,

$$AN = ND = MN = a,$$

$$\text{and} \quad BM = MC = AD = 2a.$$

$$\text{Let} \quad MO = NE = x.$$

We shall first derive an expression for the number of molecules which enter through BC and pass out through AD. There are two cases to consider.

(a) For points under AD.

For such points $-a < x < a$.

It can easily be shown that in this case only molecules whose directions are included in $\angle AOD$ pass out through AD from the element dx at O, the rest being reflected through BC.

$$\begin{aligned}\text{But} \quad \angle AOD &= \angle AOE + \angle DOE \\ &= \alpha_1 + \alpha_2.\end{aligned}$$

And from (2) the number of molecules passing through the element dx (determined by x and $x + dx$) and out through AD is

$$n_2 dx = N(\sin \alpha_1 + \sin \alpha_2) dx dt.$$

For $x > 0$,

$$n_2 dx = N \frac{(a+x)dx dt}{\sqrt{a^2 + (a+x)^2}} + N \frac{(a-x)dx dt}{\sqrt{a^2 + (a-x)^2}}.$$

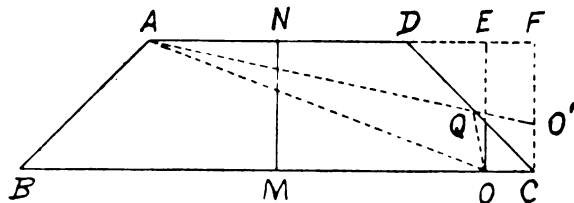
Integrating, the number of molecules passing out through AD from points under AD is

$$\begin{aligned}\int_{-a}^a n_2 dx &= 2 \int_0^a n_2 dx \\ &= 2Ndt \left[\sqrt{a^2 + (a+x)^2} - \sqrt{a^2 + (a-x)^2} \right]_0^a \\ &= 2Na(\sqrt{5} - 1)dt. \quad \dots \dots \dots (3)\end{aligned}$$

(b) For points under the sides

AB and CD, i. e. $|x| > a$.

Fig. 3.



In fig. 3 let O' be the reflexion of O in CD , and Q the intersection of CD and $O'A$. Then $\angle AQD = \angle CQO$.

It is easily seen that only molecules whose directions are included in $\angle QOA$ pass out through AD from O.

Since $\angle BCD = 45^\circ$,

$\angle O'CO = 90^\circ$,

and

$DF = a$.

Let OE be normal to BC.

Then $\angle QOA = \angle AOE - \angle QOE$.

But $\angle QOE = \angle O'AF$;

hence $\angle QOA = \angle AOE - \angle O'AF$.

$$\equiv \alpha_1 - \alpha_2.$$

Hence in this case

$$n_2 dx = N(\sin \alpha_1 - \sin \alpha_2) dx dt ;$$

and for $x > a$.

$$n_2 dx = N \frac{(x+a) dx dt}{\sqrt{a^2 + (x+a)^2}} - N \frac{(x-a) dx dt}{\sqrt{9a^2 + (x-a)^2}}.$$

Integrating, the number of molecules passing out through AD from points for which $|x| > a$, i. e.

$$\begin{aligned} 2 \int_a^{2a} n_2 dx &= 2N dt \left[\sqrt{a^2 + (x+a)^2} - \sqrt{9a^2 + (x-a)^2} \right]_a^{2a} \\ &= 2Na dt (3 - \sqrt{5}). \end{aligned} \quad (4)$$

Hence, adding (3) and (4), the number of molecules passing upward through AD is $4Na dt$.

From (2) the number of molecules passing from one side to the other is

$$2N dx dt \sin \frac{\pi}{2} = 2N dx dt.$$

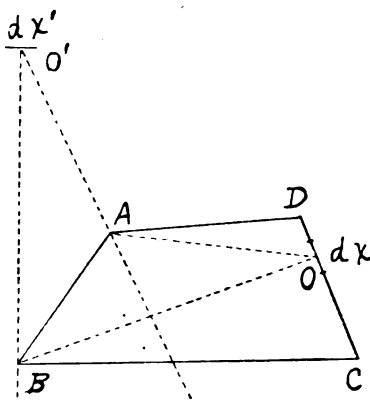
Hence the number of molecules passing downward through AD is also $4Na dt$.

This shows that the same number of molecules pass upward through a vessel of the specified shape as downward.

We shall now give a proof that applies to any two-dimensional vessel ABCD where AB and CD are sides of the vessel, AD and BC being open. This will include both the vessels studied in detail by Fairbourn. Here it is necessary to consider the directional distribution of the molecules at a point. We shall say that the directional distribution of the impinging molecules is normal at a point P and within the $\angle APB$ if eq. (1) applies to an element of length dx placed at P for all molecules which impinge in directions included in

$\angle APB$, and if further the N that applies is the N for a point within the mass of the gas—*i. e.*, a point at least three or four mean free paths from the boundary of the gas. The normal directional distribution of the molecules reflected from a point on a surface is defined in a similar manner. We shall further assume that for a point on or near the boundary the directional distribution of the impinging molecules is normal at that point and within a given angle, unless there is a boundary of the gas in that angle within a radius of three or four mean free paths.

Fig. 4.



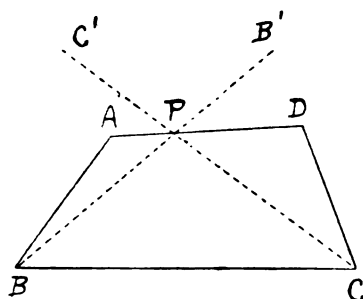
Of the molecules entering $ABCD$, some collide with the sides, some pass through without collision, but only a negligibly small number collide with other molecules.

Let us consider first those that impinge on the sides AB and CD in fig. 4. We wish to determine the number of molecules that enter through AD and collide with the sides as compared with the number that pass out through AD after reflexion from the sides; likewise for BC . In doing this we must be careful to count every molecule, and not to count any molecule more than once. It is evident that every molecule that impinges on a side will impinge for a first time after entering the vessel, and for a last time before leaving the vessel. Therefore, if at any given point of the sides we count only the molecules which enter directly or leave directly, we shall count all, and not count any more than once.

In fig. 4 consider an element dx at the point O on the side CD . Of the molecules leaving dx , all ultimately get out

through AD and BC, some directly, some only after a number of reflexions. For the sake of simplicity, suppose that all escape after no more than one reflexion, and that all the reflected molecules get out through BC. Since every path is reversible, this argument shows that molecules will strike dx in all possible directions. We shall now show that the directional distribution of the molecules impinging on dx is normal. Since $\angle AOB$ and $\angle COB$ face the free gas, it is easily seen that in these angles the directional distribution of the impinging molecules is normal. To determine the directional distribution at O in $\angle AOB$, consider dx' the reflexion of dx in AB. Since any path in $\angle AO'B$ which would lead to dx' at a given inclination to its normal if AB were not present leads to dx at the same inclination to its normal, it is easily seen that the directional distribution in $\angle AOB$ at O is the same as it would be in $\angle AO'B$ at dx' if AB

Fig. 5.



were removed. But the latter directional distribution would be normal since the angle faces free "space." Hence the directional distribution of the molecules impinging at O is normal in the entire $\angle DOC$. But regular reflexion on a plane leaves a normal distribution normal. Hence the same number of molecules return from dx through AD as entered through AD and impinged on dx . Since this is true for every elementary length on AB and CD, it follows that of the molecules impinging on the sides the same number go out through AD as entered through AD; likewise for BC.

Of the molecules that pass through but do not collide with the sides, all pass through AD. Consider an elementary length dx at P on AD in fig. 5. Only molecules whose directions of motion lie in $\angle BPC$ or $\angle B'PC'$ pass through without collision with the sides. Since these angles facing free "space" are equal and similarly situated with respect to dx , it follows that the same number of molecules leave through

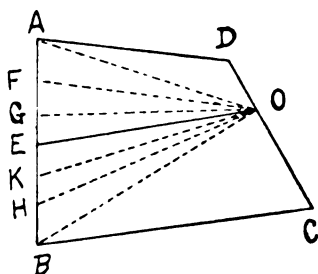
AD without collision with the sides as enter through AD and do not collide with the sides.

It follows, then, that the same number of molecules leave through AD as entered through AD, and likewise for BC.

It is easily seen that, by taking into consideration the velocities of the molecules, the argument above will show that the pressure at every point on AB and CD is the same as the pressure at any point within the mass of the gas—*i.e.*, at a point more than three or four mean free paths from the boundary. In other words, the pressure is normal at all points on the sides of the vessel.

It is evident that the same process of reasoning can be applied in the case where some molecules escape from the vessel only after a number of reflexions. Consider first the molecules that collide with the sides. Thus, if fig. 6 represents the general case, we can say that of the molecules leaving the element dx at O some ultimately go out through

Fig. 6.



AD, the remainder through BC. Furthermore, we can divide up the straight angle DOC into angles AOD, FOA, COB, etc., such that all the molecules leaving the element dx at O in directions included in any one of these angles will suffer the same number of reflexions, and ultimately go out through the same open face. To be definite, let us say that all the molecules leaving O in directions included in $\angle DOE$ escape through AD, those in $\angle AOD$ directly, those in $\angle FOA$ after one reflexion, those in $\angle FOG$ after two reflexions, etc., while below in like manner all the molecules leaving O in directions included in $\angle COE$ go out through BC, those in $\angle BOC$ directly, those in $\angle HOB$ after one reflexion, etc. Since every path is reversible, all molecules impinging on the element dx at O within any one of these angles will have undergone the same number of reflexions, and have entered through the same open face. Now, just as in the case of one

reflexion we showed that the directional distribution of the molecules impinging at O was normal, so it can easily be shown that for any number of reflexions the directional distribution of the impinging molecules will be normal at O. Having shown this, the rest of the argument follows as before.

It is easily seen that the same sort of argument applied to any point within the vessel ABCD will show that the gas-pressure and directional distribution of the molecules is also normal at that point.

So far, the argument has been confined to two dimensions. It is easily seen, however, that the process of reasoning, using the method of reflexion applied in the last two cases, could be applied to a three-dimensional vessel of the shape of a truncated pyramid, the upper and lower bases being open. It could, therefore, be applied to a vessel of the shape of a truncated cone, since the latter could be regarded as the limiting case of a truncated pyramid of many sides.

We have demonstrated, therefore, that for the type of vessels considered in this paper there is no movement of the gases in one preponderating direction. Furthermore, the type of reasoning applied above to the vessel in fig. 6 could be applied to vessels of various shapes; and it is highly probable, therefore, that there is no shape of vessel that will produce a movement of the gas in one preponderating direction.

The author acknowledges his indebtedness to Professor C. B. Bazzoni, who suggested this investigation.

XIV. *Ultimate Rational Units.*

By NORMAN CAMPBELL, *Sc.D.**

SUMMARY.—The paper contains a criticism of Prof. Lewis's theory of "ultimate rational units." It is argued that the theory is demonstrably false, and arises merely from a failure to observe that the equations by which Planck proposes to determine his "natural units" from universal constants are usually indeterminate.

After the proof is completed a few general observations are offered on the assumptions and arguments on which the theory is based

1. **T**HE theory of ultimate rational units was propounded by Prof. G. N. Lewis† in the *Phys. Rev.* iii. p. 92 (1914); extended in *J. Amer. Chem. Soc.* 44, p. 1008 (1922);

* Communicated by the Author.

† Since in the last paper Prof. Lewis takes entire responsibility for the theory, I have omitted all reference to those with whom he was associated in the earlier publications.

and re-stated in *Phil. Mag.* xlv. p. 266 (1923). These papers will be denoted as (I), (II), (III). I propose to criticize this theory; and at the outset would offer some apology for occupying valuable space with purely destructive arguments which are, moreover, belated.

My apology is that the need for criticism has only arisen recently. It has always appeared to me that the arguments on which the theory is based are utterly unsound; but for many years, since nobody seemed to take the theory seriously, I imagined that others shared my opinion. But it now appears that the very simple fallacy on which the theory is based is not generally understood. Mr. Dushman* has recently taken the theory quite seriously in interpreting some valuable experiments; Prof. Lewis has challenged criticism by re-stating his theory in a very positive manner in (III); and—most significant of all—"O. J. L.," in appending to this last paper some general objections to Prof. Lewis's arguments (in which I concur entirely), has omitted to draw attention to the simple reasoning whereby it can be demonstrated to be false.

One further word of explanation. The theory of U.R.U. (if I may use the abbreviation) is concerned with units and dimensions. In my 'Physics' I ventured on some criticism of the current exposition of this subject. It is important, therefore, to insist that the arguments I am about to advance have nothing whatever to do with any new or unorthodox views. They are all implied by the well-known reasoning on which Planck based his "natural units"; in fact, I should gather from Planck's exposition of that subject that he judged the errors which have led Prof. Lewis astray too obvious to be worth noticing explicitly. It is only when, by the most strictly orthodox reasoning, I have disposed of U.R.U., that I shall offer a few general remarks which may be (though they should not be) slightly less familiar.

2. The theory of U.R.U. is stated thus by its author:—(III, p. 270) "There is possible a set of units in terms of which all universal constants (and not merely those which are employed in defining the units) will be reduced to simple numbers." I admit at once that the theory, expressed in this form, is not demonstrably false; indeed, at some time in the future it may appear obviously true (see p. 172 below). But that is only because there is ambiguity in the terms "all universal constants" and "simple numbers." The first ambiguity

* S. Dushman, *Phys. Rev.* xxi. p. 623 (1923).

we shall find not directly important for our purpose ; but we must have some clear idea of what numbers are simple. We can gather enough indication from Prof. Lewis's use of his theory. He deduces from it the proposition that, if a set of units are chosen so that some universal constants are represented by certain simple numbers, then there is a presumption that any other universal constant is to be represented in terms of these units by a simple number, and that therefore evidence can be produced for a universal constant having one value rather than another. This last conclusion does not follow unless it is asserted of simple numbers (1) that not all numbers are simple, (2) that the simplicity of a number is something that can be determined before it is known whether it is actually the value of a universal constant. If these propositions are admitted, we know enough about simple numbers to proceed with our proof.

3. Let us proceed to discuss generally how a set of units may be chosen to give universal constants assigned values. We shall assume nothing more than the elementary principles of the most orthodox theory of dimensions, according to which there are certain fundamental magnitudes, f in number, the units of which may be fixed independently of each other, while all other magnitudes (including the n universal constants) have dimensions in terms of these magnitudes. What precisely is meant by the latter part of this assertion is best described by the equations (1) which we are about to state.

Let $U_1, \dots, U_f$ be the fundamental magnitudes, $A_1, \dots, A_n$ the universal constants. Let $a_1, \dots, a_n$ be the numerical values of these constants in terms of the fundamental units by means of which they have actually been measured ; this set of units will be termed "practical units." (*E.g.* if A_1 is the velocity of light, and c.g.s. units are practical units, $a_1 = 3 \times 10^{10}$.) Let $a'_1, \dots, a'_n$ be the numerical values which it is proposed to assign to the universal constants in the hope of finding some set of units which will give these values. If such a set can be found, let $u_1, \dots, u_f$ be the numerical values of these fundamental units in terms of the practical units. Further, let d_{rs} be the dimensions of A_r in terms of U_s . Then, in virtue of the principles assumed, there must be a relation between the numerical values and the

The condition is that there shall be some solution of equations (2), *i. e.* some set $p_1, q_1, \dots, s$ which satisfy them. The result important for our purpose is that if $n=f+n'$, where n' is positive, there are at least n' solutions, no one of which can be deduced from the others. If n' is negative or zero, there may or may not be a solution. This result would fail only if equations (2) were not independent, and if there were some necessary relations between $p_1, q_1, \dots, s$; that is to say, only if there were some dimensions which a universal constant could not have. So far as I am aware, neither Prof. Lewis nor anyone else has suggested a possible limitation on the dimensions of universal constants; the matter need therefore not be discussed. But it may be well to remark that, if there is a limitation, it is still possible to prove that U.R.U. is false in all the applications which have been so far made of it.

If n' no-dimensional magnitudes (and not only 1) can be formed of the n constants, these being independent in the sense that none of the no-dimensional magnitudes can be formed by simple combination of the others, then there will be no solution of (1) unless n' equations of the form (3) are all true; and if they are true, then the number of equations (1) is effectively reduced to $n-n'$ *.

4. With these considerations as a guide, we can state exhaustively what conditions can occur when we try to determine a set of f units by assigning values to n constants, and whether, in each of them, the determination is possible.

I. It is impossible to form a no-dimensional magnitude from the n constants.

a. $n > f$. The case cannot occur.

b. $n = f$. A single set of units can be determined, whatever values are assigned to the constants.

c. $n < f$. Infinitely many sets of units will give the assigned values, whatever they may be.

II. It is possible to form n' no-dimensional magnitudes, but the values assigned to the constants are such that one or more of the resulting equations (3) are not true.

No set of units will give the assigned values.

* The purely algebraic argument may be found difficult by some readers. But they will speedily find out the significance of what has been said if they will try to determine a set of units of mass, length, time which will give assigned values (say unity) to the 3 constants, ϵ, h, c , which form the no-dimensional combination $\epsilon^2 h^{-1} c^{-1}$.

III. It is possible to form n' no-dimensional magnitudes, and the values assigned are such that all the resulting equations (3) are true.

- a. $n > f + n'$. The case cannot occur.
- b. $n = f + n'$. A single set of units can be determined, whatever values are assigned to $n - n'$ of the constants, those assigned to the remaining n' being such as to make the n' equations (3) true.
- c. $n < f + n'$. Infinitely many sets of units can be determined, whatever values are assigned to $n - n'$ of the constants.

For completeness a word should be added about experimental error. The numerical values $a_1, \dots, a_n$ are, of course, never known exactly; equations (1) and (3) should be replaced strictly by inequalities assigning limits. The effect of such a substitution on the conclusions just stated would be to replace in I. *b* and III. *b* "a single set of units" by "a single set of ranges within which the units must lie." But conciseness and no inaccuracy follow from the neglect of this complication.

An examination of our conclusions shows that, in deciding what set of units, if any, will give assigned values to universal constants, it cannot possibly be relevant whether those values are simple. For if the conditions are such that a set can be determined uniquely at all, there are either no limits on the choice of assigned values (I. *b*) or the limits are imposed by equations, involving experimental values, which cannot be judged to be true or untrue before those values are known. There is no room anywhere for the conception of simple numbers, which are a special class recognizable before the experimental determination is complete. While therefore we have to admit (owing to the vagueness of the terms involved) that it is impossible to prove that U.R.U. is not true, we can assert that, if it is true, it is equally true when for "simple" we write "simple or not simple." Accordingly it cannot possibly afford any justification for any kind of presumption that any numerical value is likely to be simple rather than not simple.

5. With that proof my main task is accomplished. But before proceeding to more general matters, it may be well to classify according to the table just given the cases considered by Prof. Lewis. But before this can be done, some preliminary observations are necessary.

It is remarkable that the author of U.R.U. does not profess to have determined the set of units which make all universal constants simple numbers. The omission may seem significant; for it might be thought that, if the theory was true, it would be merely a question of a little arithmetical labour to give this, the most convincing, proof of it. But this criticism of Prof. Lewis's work would overlook the difficulty of deciding what numbers are simple according to his ideas. I have not been able to discover exactly what his views on this subject are; and, since they seem to lead to some surprising conclusions, it is fortunate that it is possible to prove U.R.U. to be false without coming to any very exact decision on the matter. But this difficulty (or possibly some other), which has prevented him from taking the obvious course, has led to a curious procedure. He has taken throughout the centimetre as the unit of length and assigned values to universal constants so as to determine the other fundamental units. Here again is a difficulty in the argument which again, fortunately, we are able to avoid; for it is by no means clear how many fundamental units (or magnitudes) Prof. Lewis thinks there are. His practice would seem to indicate that he takes the conventional view that there are 4, namely length (l), time (t), temperature (θ), and either mass (m) or energy. But his deliberate statements would seem sometimes to suggest that he thinks that we have some choice in the matter, and that we might, if we pleased, take only one fundamental magnitude. This doubt does not affect the proof that has been given; for that proof holds whatever value is assigned to f . But in order to classify his instances it is convenient, and will save much discussion, to come to some decision on the matter. I shall assume that there actually are four fundamental units; that choice will offer the greatest chance of making his arguments intelligible to the many others who take that view*.

If, then, there are 4 fundamental units and Prof. Lewis chooses arbitrarily the centimetre as one of them, he has three to determine. In his first application of U.R.U., in order to determine these three, he assigns values to 4 universal constants, namely c (velocity of light), k (Boltzmann constant), e (electronic charge), a (Stefan's constant).

* As it happens, I agree with Prof. Lewis in holding that the assertion that there are 4 fundamental units is an inadequate way of expressing the facts, although, if reasonable care is taken, it does not lead often to actual error. But while he wants to reduce the number of fundamental magnitudes, I want to increase it.

This last constant he defines, in a rather unusual manner, by the relation $E = a \cdot V \theta^4$, where E is the energy in volume V in the interior of a black body at temperature θ . One and only one combination of these constants is no-dimensional, namely $a \epsilon^6 k^{-4}$. Accordingly $f=3$, $n=4$, $n'=1$. His case can be made to fall under III. *b*, and he can define his three fundamental units unambiguously whatever values he assigns to his constants, so long as these values are consistent with the single condition $a \epsilon^6 k^{-4} = a' \epsilon'^6 k'^{-4}$. Within experimental error $a \epsilon^6 k^{-4} = (4\pi)^{-6}$; so the values he chooses, namely $c' = k' = a' = 1$, $\epsilon' = \frac{1}{4\pi}$, will suffice. But infinitely many other sets of values would serve equally well.

In his second application (II.) his constants are c , k , ϵ , C_1 . C_1 is a constant defined by an equation due to Sackur, relating to the entropy of a monatomic gas. It has the dimensions $m^{-3/2} l^{-3} \theta^{-3/2}$, and $C_1 = 3.3 \times 10^{-3}$ (about). Here again there is one and only one no-dimensional combination of the constants, namely $c^6 k^3 \epsilon^{-12} C_1^{-2}$. The case again can be made to fall under III. *b*. The values assigned to c' , k' , ϵ' are the same as before; the simple value he assigns to C_1' is $N^{-5/2}$, where N is the number of molecules in a gram-molecule*. Since within experimental error

$$c^6 k^3 \epsilon^{-12} C_1^{-2} = (6.2 \times 10^{23})^5 \times (4\pi)^{12},$$

the values will serve to determine the 3 units, but so also will infinitely many other sets of values.

If the two instances are combined, we have $n=5$, $f=3$. But no further independent no-dimensional combinations are introduced. ($c^6 k^{-5} a^2 C_1^{-2}$ and $c^{-24} a^{-3} \epsilon^{30} C^8$ are no-dimensional, but they result from combination of the two original no-dimensional magnitudes.) Accordingly $n'=2$, and the retention of the same values assigned to the constants brings the instance again into III. *b*.

* Here I cannot refrain from inserting one numerical criticism, although, as I have explained, it has nothing to do with my main thesis. It is surely remarkable that the number of molecules in a *gram-molecule* should be a simple number in whatever units we choose to measure mass. Can Prof. Lewis and his associates in this part of his work have overlooked the fact that in assigning to C_1 the value $N^{-5/2}$, they are assigning a value which they must retain whatever unit of mass results from that assignment? It is only if the gram results as the unit of mass that the value of C' will be a simple power of the number of molecules in a quantity of the gas having M times unit mass, where M is the molecular weight. The arguments offered for the simplicity of this value are quite beyond my comprehension. But, once more, even if they are perfectly sound, that does not affect the falsity of U.R.U.

6. The fact that all instances fall in this class suggests how Prof. Lewis may have been led astray. In hazarding this guess, I am obviously taking a risk; and if Prof. Lewis denies that such was his train of thought, I have no defence to offer. But to indicate how the fallacy might have been reached may perhaps save others from the mistake. I suggest then that he started with a belief in U.R.U. He found that if the constants he chose for discussion (I cannot suggest why he originally chose so curious a constant as his α) were to determine any set of units at all, the values he assigned to them must satisfy equation (3). He found that he could assign simple values which would satisfy equation (3). He concluded, with perfect logic, that U.R.U. could not be true unless the constants had these simple values; in the technical sense, U.R.U. "implies" that the constants have these values. But he overlooked the well-known fact that a false proposition implies all propositions, true and false. He could not at the same time prove both that U.R.U. was true and that the constants had these values. Indeed, if he had not been obsessed by his belief in U.R.U., he would have observed that there were infinitely many sets of values assigned to his constants which would enable him to determine from them a set of units. This fact, if he had observed it, strongly suggests that U.R.U. is false; for U.R.U. suggests that the set ought to be unique. The argument therefore is not analogous to one with which he may have been inclined to compare it. If I invent a theory (say Planck's theory) which predicts that a numerical relation holds between universal constants (say $h^3 = \frac{8\pi^9 k^4}{15c^3 a}$), and if I find that the experimental measurements are consistent with this relation, then I am apt to conclude both that the theory is true and that the magnitudes are connected exactly by the relation. The argument—though I would not throw the slightest doubt on its validity—is logically inadmissible on account of the universal implication of false propositions. But there is a very essential difference between this argument and that which I am venturing to impute to Prof. Lewis—namely, that in the sound argument there is nothing, and, from the nature of the argument, can be nothing, in the conclusion which throws doubt on the premisses.

7. On this view Prof. Lewis's error arose from his presumption that U.R.U. was true. How came he to entertain at all a theory so easily demonstrated to be false? He seems to have told us; he apparently believes that by some juggling

with dimensions he can rid science of all "arbitrary" numbers. This belief is, of course, directly contrary to the views that most of us hold ; but if it can be seriously entertained, it may not be a waste of time to inquire once more into the nature and source of the arbitrary element in all measurement.

Consider first fundamental * measurement, the process by which we assign numerals to represent properties (magnitudes) without making use of a similar process previously established for other properties. The possibility of measuring a magnitude fundamentally depends on the truth of certain laws. The form of these laws is such that, while it is necessary to measurement that we assign the numeral 1 to one of the systems having the magnitude, it is immaterial to which of the systems we assign that numeral ; whichever system we select as a unit, we can still measure all of the remaining systems. That perfect liberty of choice is a consequence of the form of the laws ; if the laws were other than they are, it is possible that we might have to adopt some other kind of measurement in which we should not have that liberty. But we have to take laws as they are. Prof. Lewis says that "there is nothing nature abhors more than an arbitrary number" ; but (to retort in his own phraseology) it is nature herself who, by framing laws as she has framed them, forces this arbitrary choice upon us.

In one respect it may seem that the statements just made need modification. There are certain magnitudes (or it may be so admitted here) which, when we have measured them, turn out to be all integral multiples of a single unit. Now, if we only developed our system of measurement so far as to permit of the measurement of integral multiples of the unit, and if we made use only of the laws which permit this development, then there would truly be a limitation in the choice of unit. Unless we chose our unit in a certain way, we should not be able to measure all the systems having the magnitude ; we should have no choice if we were to measure completely. But there is no reason why we should stop the development of measurement at this point ; even when these magnitudes are concerned, the laws which permit fractional measurement are still true ; and if we make use of these laws, as we do with other magnitudes, we have still complete freedom in the choice of unit. Even here, where, as Prof. Lewis would say, nature might reasonably have limited our choice, she still prefers to leave it unlimited.

* I am using the term fundamental here in the sense explained in 'Physics,' Ch. x.

It follows that the statement that any fundamental magnitude has any particular numerical value is arbitrary, in the sense (I shall always use the word in this sense hereafter) that the statement does not imply any law or fact*. It implies nothing about the laws or facts of measurement, except that these are of a certain form which is common to all such laws and facts; it cannot imply any other law, for the statement can be made when no laws except those of measurement are known. All the laws involving the numerical values of magnitudes are laws relating two or more numerical values.

We must now turn our attention to these laws, for on them depends derived measurement. The important question here is whether anything is altered in these laws by the change in the numerical values of fundamental magnitudes which is consequent on a change in the unit; for, if anything in the law is altered, or if by a change of units any law can become true which was previously false or *vice versâ*, then, and only then, does the choice of unit cease to be arbitrary. The question can be answered only if we are quite clear what these laws state. Suppose we are comparing the weight and the volume, both measured fundamentally, of different lots of water at 4°C . Then, if we adopt as our fundamental units the gram and the c.c., we shall find the law that the weight is always equal to the volume. If we adopt any other units, this law will not be true; but we shall have in its place the law that the weight is proportional to the volume, the constant of proportionality varying with the units. Now, is a law involving equality different from a law involving proportionality, or a law involving one constant of proportionality different from one involving another? If it is, then the law to be stated varies according to the fundamental units we adopt, and the choice of those units is not arbitrary; the choice determines the law. Perhaps Prof. Lewis or some other will say that laws of equality and of proportionality are different; let us examine the consequences of such a decision. The numerical law in question defines the derived magnitude density; if that law is not true, there is no such thing as the density of water at 4°C . If, then, the law is true when we choose one pair of units (A) and not when we choose another (B), water has a density in one case but not in the other. But now let us examine water at 0°C . According to the decision we have taken, water has no density if we choose the units A; for the relation

* The distinction between a fact and a law is discussed in 'Physics,' pp. 81-87.

between weight and volume is no longer equality; if we retain the same units, there can be no meaning in the statement that the density of a substance varies with its temperature. Such a statement has meaning only if we adopt one of two courses. Either we must admit that the law relating weight and volume, and therefore the meaning of density, is unaltered when the relation of proportionality is substituted for that of equality or the factor of proportionality otherwise changed; or we must measure every density in terms of different units, the numerical value of density being always the same. The second alternative is clearly fatal to Prof. Lewis's contention that there is one system of units preferable to all others on the ground that it removes arbitrary values; only the first (which, of course, is that universally adopted) need be considered. But if we adopt this first alternative, the law defining density will remain true whatever units we choose for measuring weight and volume; and we must conclude that in the statement of numerical laws and in derived measurement, so intimately connected with that statement, the choice of units is arbitrary in the sense that the truth or falsity of laws is unaffected by such choice. For exactly the same argument might be repeated for a numerical law involving numerical relations other than simple proportionality.

This, then, is our conclusion—it is trite enough. Whether we are speaking of fundamental or derived magnitudes, the statement that the magnitude characteristic of any system has one particular numerical rather than another is arbitrary; it does not imply a law or anything that is scientifically true. A law is implied in the statement that the magnitude is measurable; a law, or at least a fact, is implied in the statement that there is a numerical relation between one magnitude and another or, in particular, that a magnitude has a particular value in terms of stated units. But if anything beyond these statements is contained in the assertion of a particular numerical value, that something is not a scientifically significant proposition. And since change of units affects nothing but numerical values and leaves statements of the kind mentioned unaffected, any scientifically significant proposition which can be stated in terms of one set of units can be stated equally well in terms of any other. The choice of the units in which we state our laws will always remain arbitrary, unless the nature of those laws is profoundly changed.

8. So much for Prof. Lewis's presumption. I do not propose to examine his arguments; for that would lead us

into a discussion of the whole theory of dimensions, of which I have said enough elsewhere *. But to him, and to others who attempt to prove scientifically significant propositions by changing the dimensions conventionally attributed to derived magnitudes, I would suggest a dilemma. Either the statement that such a derived magnitude (*e.g.* velocity) has the conventional dimensions (*e.g.* lt^{-1}) is the expression of some scientific law or fact; or it is not. If it is such an expression then, unless the statement is actually untrue (a view not usually urged by those I am addressing), nothing true can be deduced by denying it. If it is not such an expression, but is a mere convention, then it is impossible to deduce from it anything scientifically significant, whether true or not.

9. Having contested so many of Prof. Lewis's assumptions and arguments, I cannot leave the matter without inquiring finally whether there is any grain among the chaff, and whether the facts to which he has drawn attention can be made the basis of any important conclusions. The new facts which he has brought to light are, so far as I can see, only two; namely that, within experimental error, $k^4 e^{-6} a^{-1} = (4\pi)^6$ and $(\frac{1}{2} e^{12} k^{-3} c^{-6} = (4\pi)^{12} N^2$. Prof. Lewis says that it would be a "bizarre coincidence" if these numerical agreements were insignificant. Can we agree with him? I think this question can be answered if we return and ask once more: What are "simple" numbers, and why do we attach importance to them? †.

Prof. Lewis opens his paper (III) by speaking of "simple numbers like 2 and π ." It is clear, therefore, that in his view (in which I concur) physically simple is not the same thing as mathematically simple; for mathematically these numbers are almost as diverse as they can be; they resemble each other in nothing but being real. His view is more positively indicated in (I), where he argues that π is a simple number because it is important in geometry. If we ask why a number should be simple as a value for the electronic charge, because it is important in geometry, surely the only answer can be that it is simple because geometrical concepts are involved in all our laws and theories, whether they concern electrical or any other magnitudes. If this is so, the answer we must give to our questions is that values of magnitudes are simple when we hope or expect to be able to produce some law or theory to explain why the magnitudes have those values; and that the importance of simple numbers

* 'Physics,' Chs. xiv., xv.

† Cf. 'Physics,' pp. 431-434.

lies in the laws or theories which may explain them. That is the only answer I can find; and I am inclined to think that Prof. Lewis would accept it.

If we accept it, Prof. Lewis's contention that it cannot be a mere coincidence that $k^4 e^{-6} a^{-1}$ coincides so nearly in value with the simple number $(4\pi)^6$, and that therefore it must have exactly this value, should be interpreted to mean that he is confident that a theory can be produced (for a proposition connecting universal constants cannot be a law) to explain why $k^4 e^{-6} a^{-1}$ has this value, and that he is equally confident that none could be produced to explain why it has any other value lying equally within the range of experimental error of the measured value. But if this is his contention, it would be strengthened enormously if he could give some indication of what his theory is, and of why he is so sure that any theory leading to another value within the range is impossible. His position is entirely different from that of those who have produced actual theories which lead to numerical coincidences; it is infinitely weaker. And it is especially weak as regards its negative element: for the most surprising conclusions concerning simple numbers have turned out to be true. Thus, Planck's theory leads to the conclusion that $\frac{8\pi^6}{15}$ is a simple number in this sense, being involved in a theoretically explicable relation between universal constants*; while, on the other hand, since the relation which was at one time suggested, $\frac{(4\pi\epsilon)^2}{c} = \frac{h}{2\pi}$, turns out not to be true, $(4\pi)^2$ may not be a simple number. Probably we should all agree with Prof. Lewis if he asserted that some theory would be found some day which would connect together all of the universal constants between which no relation is known at present, and that this theory would introduce powers of π as a simple constant. But when he asserts that this constant must be $(4\pi)^6$ and no other (which does not differ greatly), he must pardon us if we do not share his confidence.

Lastly, if the day comes when such a theory is propounded, the theory of U.R.U. will at last be triumphantly established. For any set of units will give to all universal constants some values, and, whatever those values may be, they will be simple! The theory will be true,—but it will be useless.

Sept. 8, 1923.

* Prof. Lewis does not, or did not, accept Planck's theory (Phys. Rev. 4, 331, 1914). But he proposed an alternative theory to take its place; and this theory would presumably give the same value for the constant in the relation between a , h , k , c .

XV. *The Resistance of Air to Falling Spheres.* By
ROBERT G. LUNNON, M.A., M.Sc.*

I.

IT is well known that considerable disagreement exists as to the proper value of the constant ϕ_1 in the equation of fluid resistance for considerable speeds,

$$R = \phi_1 \rho d^2 v^2$$

where ρ is the fluid density, d the diameter (or some other length measurement) of the body, and v the uniform velocity. Results for spheres have been collected by Pannell † and by Schmidt ‡, and the values of ϕ_1 range from ·08 to ·28. A later value by L. F. Richardson § is ·17, and another recent result, by Cooke ||, gives ·24. These figures refer only to those relatively high speeds for which ϕ_1 is supposed to be constant. For lower values, ϕ_1 is usually compared with a second quantity of zero dimensions, the Reynolds number $\phi_2 = v d \nu^{-1}$, where ν is the kinematic viscosity, the quotient of the ordinary viscosity by the density. The proper form of the $\phi_1 \phi_2$ curve is also a matter of uncertainty (see Pannell's report ¶ and the Enc. of App. Physics, vol. i. p. 369). Further, the conditions with non-uniform velocities have been examined only by Schmidt **, for low velocities, except for certain data recorded by Allen †† and by Shakespear ‡‡. The measurements to be recorded in this paper were made with the object of obtaining more light on these three problems.

II.

Measurements have been made of the times of fall of spheres of various sizes and densities for distances up to 600 metres in the shafts of four coal-mines in this district, and also, for shorter distances, in the tower and laboratories of this College. In the mine-shafts the balls were released by an assistant in the cage, which was set at different heights for successive experiments, and were received in a suitable truck or enclosed space at the shaft bottom. In some cases

* Communicated by the Author.

† Pannell, Adv. Ctee. for Aeronautics, Report No. 190 (1914).

‡ Schmidt, *Ann. der Physik*, lxi. p. 633 (1920).

§ L. F. Richardson, *Phil. Trans. A*, 223, p. 351 (1923).

|| Cooke, *Phil. Mag.* xxxix. p. 350 (1920).

¶ *Loc. cit.*

** *Loc. cit.*

†† Allen, *Phil. Mag.* l. pp. 323, 519 (1900).

‡‡ Shakespear, *Phil. Mag.* xxviii. p. 728 (1914).

the times of release and of striking were recorded by electromagnetic arrangements similar to those described by Shakespear*, with the addition of a tape-machine or a chronograph. More often, in the pits, the release alone was electromagnetic, and the time of striking, as heard, was measured by a special stop-watch. In a few cases the ball was dropped by hand and the time of release signalled by sound to the recorder below, a correction being then made for the speed of sound. Usually five balls of the same size were dropped consecutively, and from the concordance of their times, and also of the times in different pits, after allowance for air-currents, it appeared that the errors did not exceed one-fiftieth of a second for times up to 6 seconds, and one-tenth for times up to 15 seconds. Some of the conditions in the pits were particularly difficult, and this degree of exactness was considered satisfactory.

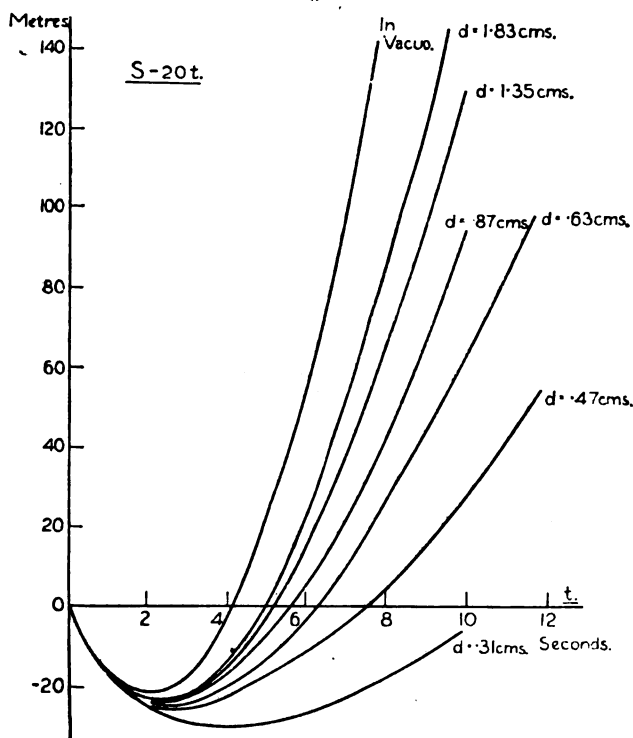
Polished steel balls were chiefly used for the experiments. These were of fifteen different sizes, varying from 0.24 cm. to 1.83 cm. in diameter, and were of density 7.72 grams per cm.³: the actual measurements are recorded in Table III. The corrected results for the relation between time of fall and distance are given in fig. 1 and in Table II. These refer to a few of the sizes only, for the sake of simplicity, and the results for the remaining sizes may be easily calculated from the formula given hereafter. The actual distances through which the falls were timed were (in metres) 568, 456, 346, 115, 88, 49 in pit W, 320 in pit H, 309, 247, 181, 117, 62 in pit U, 126, 110, 92, 73.5, 55.2, 35.1, 17 in pit B, and several distances less than 25 metres in the College buildings. Some 500 measurements in all have been used in obtaining the figures of Table II. and the graphs of fig. 1. It is to be noticed that fig. 1 does not show the relation between distance (s) and time (t) directly, for the (s, t) curves are not clearly separable on any convenient scale. It is convenient to plot $s - 20t$, where s is in metres, against t , and the values of s for any given values of t may easily be calculated after a reading of the graph.

In the results thus shown, the actual observations are not given, but their values corrected for standard conditions. The chief correction is that needed on account of the air-currents in the pit-shafts. These troublesome currents cannot be avoided, for forced ventilation is continuous in most mines, and even when the driving-fan can be stopped, there is a certain amount of natural draught. It was

* *Loc. cit.*

generally possible to work in sections in which the draught was uniform, and after taking anemometer measurements in each case, corrections could be made according to the theory which is developed later. These corrections were small, except for the smallest balls; and this is fortunate, because their calculation involves certain empirical constants which

Fig. 1.



can only be determined approximately from the actual results. The measurements over the longest distances, in pit W, were useless because of the great speed and non-uniformity of the air-draught, and it is hoped to repeat these elsewhere.

III.

The equation of motion for a falling sphere is

$$m\dot{v} = mg - R,$$

and if $R = \phi_1 \rho d^2 v^2 = av^2$, say, then

$$m\dot{v} = mg - av^2. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Integrating, and putting $v=0$ when $t=0$, leads to

$$v = c \left[1 - \frac{2}{1 + e^{pt}} \right] = c \tanh pt,$$

where

$$c = \sqrt{\frac{mg}{a}}, \quad p = 2\sqrt{\frac{ag}{m}} \dots \dots \dots (2)$$

This is easily integrated, and leads to

$$\begin{aligned} s &= \frac{2c}{p} \log \frac{1+e}{2} - ct \\ &= \frac{2c}{p} \log \cosh \frac{pt}{2} \quad \text{or} \quad \frac{m}{a} \log \cosh \frac{pt}{2} \dots (3) \end{aligned}$$

This formula is a cumbrous one for computation, but it has the advantage that it can be compared directly with the s, t data. Many workers have preferred to deduce the velocity from their results, and even the acceleration, but there is a risk of serious error in these deductions, and we have preferred the longer method. It was found after trial of a succession of values of c and p , that it was possible to obtain a good fit of the experimental curves with formula (3). But whereas the values of c —the terminal velocities—were proportional to $\sqrt{\frac{m}{a}}$ for different balls, as (2) indicates, the values of p were not inversely proportional to this, as in (2).

Schmidt has proposed to amend equation (1) by assuming that when v is not uniform the resistance depends upon the acceleration in this manner:

$$R = av^2 + b\ddot{v} - k\dot{v}^2.$$

For a special value of the constant k , this leads to an integrable form of the equation of motion, with the result

$$v = c(1 - e^{-qt}),$$

and hence to

$$s = ct - cq^{-1}(1 - e^{-qt}).$$

This result does not fit our experimental data better than (3), and although it offers simpler formulæ for v and s , it only does so after a special assumption.

We have therefore considered a rather simpler hypothesis, viz. that

$$R = av^2 + b\ddot{v}, \quad \dots \dots \dots (4)$$

where the constant b , like a , is proportional to the area of

the ball. This leads to the same form as the simple square law,

$$s = \frac{2c}{p} \log \frac{1 + e^{pt}}{2} - ct,$$

but in this the value of p is changed :

$$c = \sqrt{\frac{mg}{a}}; \quad p = \frac{2\sqrt{amg}}{m+b}, \quad \dots \dots (5)$$

and s may now be written

$$s = \frac{m+b}{a} \log \cosh \frac{pt}{2}. \quad \dots \dots (6)$$

The connexion between c and p is here of the form

$$p^{-1} = Ac + Bc^{-1}.$$

This relation was found to hold for the values of p and c which best fitted the experimental results, and the hypothesis (4) is therefore justified. By taking the best values for a and b , the values of p and c have been deduced for each size of ball, and formula (6) provides the means for an exact comparison of theory and experiment.

It is first necessary, however, to examine the important air-current corrections. When a ball falls against an upward current of air of n cm. per second, equations (1) and (4) must be replaced by

$$m\dot{v} = mg - a(v+n)^2 - b\dot{v},$$

and the solution of this is

$$s = \frac{2c}{p} \log \frac{1 + r e^{pt}}{1 + r} - (c+n)t, \quad \dots \dots (7)$$

where

$$r = \frac{c+n}{c-n}.$$

When the current is downward, it helps the ball until $v=n$, and for this period,

$$m\dot{v} = mg + a(n-r)^2 - b\dot{v},$$

from which there follows

$$v = n - c \left[\frac{n - c \tan \frac{pt}{2}}{c - n \tan \frac{pt}{2}} \right].$$

Hence $v=n$ when $c \tan \frac{1}{2} \theta = n$; and since n is small compared with c , we may write from this, $t = \frac{2n}{pc} = T$, say. In our experiments, T was always less than one second, and the distance travelled in this time is found, by a further approximate integration, to be $s = \frac{n^2}{pc} = S$, say.

The further motion follows the law

$$m\dot{v} = mg - a(v-n)^2 - b\dot{v}.$$

This may easily be solved, and finally we obtain for the total distance fallen,

$$s = \frac{2c}{p} \log \frac{1 + e^{pt'}}{2} - (c-n)t' + S, \quad \dots (8)$$

where $t' = t - T$, and c, p have the same meanings as before.

The expressions (6), (7), and (8) cover all the cases of our experiments. The effect of the wind, as calculated from these equations, may be seen from the following figures, referring to a steel ball of 1.11 cm. diameter for which $c = 5090$ cms. per sec., $p = .343$. They give the distances fallen in stated times—first, in still air; second, against a current of 1.8 metres per second; and third, with a current of 4.8 metres per second; these were the actual currents in two of the pits.

TABLE I.

Times of fall	2	4	6	8	10	12 seconds.
In still air	17	65	134	220	312	410 „
Against 1.8 m.p.s.	165	64	132	214	303	398 „
With 4.8 m.p.s.	18	66	140	238	333	443 „

It was found that the corrections based on these figures made a satisfactory concordance between the results of the four pits for those distances which they had in common.

The conditions of fall vary also in respect of air-density and of the strength of gravity. The variation of g with depth, as measured approximately by Airy's experiments in the neighbouring Harton pit, is much too small to affect the present results. As regards density, there was an increase in temperature of 9°C. and in pressure of 82 millibars at the bottom of the deepest shaft, and also the humidity had increased to saturation. Measurements were made in each case, and the maximum variations led to a 4 per cent. increase in density (at 600 metres), and hence to a reduction of 2 per cent. in c . It is not possible to state exactly the

effect upon the second constant p , because this depends upon b , of which the nature is unknown*. But the effect of b is small except for the smallest balls, and, apart from this, we find an increase in p of 2 per cent. for a ball of .87 cm. in diameter. These changes in c and p together, only produce an appreciable change over long distances: their effect would be to reduce the distance travelled in 10 seconds from 298 to 295 metres. The actual corrections which have been made in the following figures in no case exceed two metres.

The complete data for falling spheres in dry air at normal temperature and pressure are set out in the following table. Besides the figures derived from the experiments, there are the distances in smaller type which have been calculated from the theory.

TABLE II.

Table of Distances fallen in stated times.

Diameter...	.317 cm.	.476	.635	.873	1.110	1.349	1.650	1.826	
Mass	.129 gm.	.432	1.03	2.69	5.54	9.93	18.2	24.6	
Terminal velocity(c) }	27.1	33.1	38.3	45.0	50.9	55.8	61.8	65.1	metres per second.
p	.51	.461	.422	.378	.343	.319	.293	.280	
Distances travelled, in metres.									In vacuo.
1 second ...	...	4.3	4.4	4.5	4.6	4.6	4.7	4.8	4.90
	33	35	37	4.0	4.1	4.2	4.2	4.2	
2 seconds...	16	16.2	16.5	17	17	17.5	...	18.7	19.6
	13	14.5	15.5	16	17	17			
4 " ...	50	59	62	64	65	67	...	68	78
	47	54	58	62	65	67	68.5	69	
6 " ...	94	110	117	128	132	135	139	145	176
	92	107	117	128	134	139	144	147	
8 " ...	142	166	186	204	...	226	243	...	312
	143	167	186	206	220	231	243	245	
10 " ...	194	228	265	295	312	327	347	...	490
	197	232	260	290	312	330	347	356	
12 " ...	...	297	343	...	...	...	...	...	707
	...	298	337	378	410	438	466	476	

It will be seen that the fit of experiment and formula is a good one within the range of sizes and times dealt with. The chief divergences occur at the shorter periods, for which the present theory is not expected to be applicable. For very low speeds the resistance must follow Stokes's law; and after this stage is passed, the s, t curve must show at least one

* The dimensions of b suggest its dependence upon the volume, rather than upon the area, of the ball; but it is important to notice that the experimental results lend no support to this view.

double bend, as Schmidt's results very well show, when the first vortex ring forms and slips off behind the ball. No evidence of these initial stages can be expected from the present experiments, for they are probably completed during the first few centimetres of fall. No single formula can represent the passage of the sphere from the stage of steady, slow motion, through that which produces steadily increasing turbulence in the air, up to the final stage of "steady" turbulence. The formula we have considered is also inapplicable at the commencement of fall, because it assumes an initial acceleration of $\frac{m}{m+b} \cdot g$ instead of g ; for our equation of motion may be written thus:

$$(m+b)\dot{v} = mg - av^2.$$

The constant b appears to represent a "dragged" mass, adding to the inertia but not to the gravitational pull; but its magnitude, $\cdot 55d^2$, is much greater than can be explained on a physical basis of this kind.

The values of the constants which are found to give this best fit of experiment and formula are

$$c = \frac{2400\sqrt{m}}{d}, \quad p = \frac{2gc}{c^2 + 3,170,000},$$

and hence, from (5),

$$a = 1.70 \times 10^{-4}d^2, \quad b = \cdot 55d^2.$$

The constant a is often written $\phi_1\rho$, as above; and introducing $\rho = \cdot 00129$, we find for the resistance

$$\underline{R = \cdot 132\rho d^2v^2 + \cdot 55d^2\dot{v}}.$$

These figures refer throughout to c.g.s. units, and numerical values for c , p , and b are given in Table III.

The new value of ϕ_1 , viz. $\cdot 132$, holds for velocities from 25 to 65 metres per second, and for values of ϕ_2 between 5000 and 85,000; it is estimated to be correct within 4 per cent. It may be compared with the values $\cdot 130$ to $\cdot 150$ found by Allen for similar balls falling in water, with $\cdot 170$ found by Schmidt for lighter spheres in air and water, and with the range $\cdot 165$ to $\cdot 188$ found by Shakespear for larger and lighter balls in the air. These last results are in rough accord with our own, for Shakespear found a decrease in ϕ_1 for diminishing diameters, and an extrapolation of his formula leads to values of ϕ_1 between $\cdot 13$ and $\cdot 14$ for diameters of

a centimetre. The present experiments, however, showed no sign of variation with diameter between $d=0.4$ and $d=1.8$ cm.

TABLE III.

Diameter (cm.).	Mass (grams).	c (terminal velocity) (cm. per sec.).	p (sec. ⁻¹).	b (grams).
.238	.054	2350	.51	.031
.317	.129	2710	.51	.055
.476	.432	3310	.461	.124
.555	.692	3590	.439	.169
.635	1.03	3830	.422	.22
.714	1.47	4070	.406	.28
.873	2.69	4500	.378	.42
.952	3.48	4700	.366	.50
1.03	4.44	4900	.354	.58
1.11	5.57	5090	.343	.68
1.35	9.89	5580	.319	1.00
1.55	15.16	5970	.301	1.32
1.65	18.25	6180	.293	1.50
1.83	24.67	6510	.280	1.83

There is little basis for a comparison of the new acceleration term with the results of other workers. Shakespear deduced from his experiments that if different balls fall a certain distance in the same time, then their weights are proportional to their areas. This is in agreement with our theory; for from (5), in which a and b are proportional to the areas, it may be shown that c and p are constants if this relation holds.

The only result published by Allen for non-uniform velocities refers to a ball falling in water. With the constants in question, $d=.318$ cm., $m=.132$ gram, our theory gives the terminal velocity, c , as 91.9 cm. per sec., whereas Allen found 90.9 by experiment. To find p , we substitute the effective weight, in water, for the actual weight, in the numerator of (5), and since the dimensions of p are [time]⁻¹, no further change is needed. Calculation gives $p=.13.1$; and the theoretical curve obtained from these values of c , p is an excellent fit for Allen's measurements, as recorded.

It may be noted in conclusion that the present theory answers a question raised by Shakespear. If two spheres of different diameters are weighted so as to fall a certain distance in equal times, will they take equal times for all

other distances? We have seen that for two such balls the ratio of mass to area is the same, and hence the constant p can be expressed in terms of c :

$$p = \alpha c(\beta + c^2)^{-1}.$$

The equation of motion may therefore be written in the form

$$s = \frac{2}{\alpha}(\beta + c^2) \left[\log \left(1 + c^{\frac{\alpha c t}{\beta + c^2}} \right) - \log 2 \right] - ct,$$

and the question asked is whether the same pair of values of s and t could occur for different values of c . It seems that the members of the family of s, t curves obtained by varying c do not intersect within the region of positive values of s and t ; and we conclude that the value of c is uniquely determined by one pair of s, t values. Hence, if two balls are together at one point of their fall, after starting together, they remain together throughout.

The author's thanks are due to the managers of the Blucher, Wearmouth, Usworth and Hebburn Pits for their kindness in offering facilities and considerable help for these experiments, and to Mr. L. F. Richardson for some useful comments upon the work.

Summary.

1. The fall of small steel balls in coal-mine shafts has been investigated, and results are given, corrected, for dry, still air.
2. A value $\phi_1 = 132$ is obtained for the resistance coefficient for steady motion, for values of ϕ_2 , the Reynolds number, from 5000 to 85,000.
3. For accelerated motion, the formula

$$R = \phi_1 \rho d^2 v^2 + b \dot{v}$$

is introduced, and found to give satisfactory results after the first 2 seconds, the value of b being $\underline{.55d^2}$ in C.G.S. units, d being the diameter in centimetres.

Armstrong College,
Newcastle-on-Tyne.
Sept. 3rd, 1923.

XVI. *On Waves due to a Single Impulse in Deep and Shallow Water.* By GEORGE GREEN, D.Sc., Lecturer in Natural Philosophy in the University of Glasgow*.

THE problem of determining the wave-motion due to an initial surface elevation confined to the immediate neighbourhood of any point is fully discussed in Lamb's 'Hydrodynamics' for the case of infinitely deep water. The corresponding problem for the case of finite depth is treated by the late Lord Rayleigh in "On the Instantaneous Propagation of Disturbance in a Dispersive Medium, exemplified by Waves on Water Deep and Shallow" (Phil. Mag. xviii. 1909). The aim in view in this paper is to trace the effect of increase of depth on the wave-motion arising from a specified initial disturbance. Lord Rayleigh points out that certain gaps exist in our solutions, and that some transformation of the fundamental integral is called for. The fundamental integral has since been evaluated in the form of a convergent series by Pidduck†. In the present paper the intention is to indicate a transformation of the fundamental integral which overcomes the difficulty pointed out by Lord Rayleigh, and to discuss more fully the formation of the front for the case of waves advancing in shallow water. Professor Lamb, referring to the problem for deep-water waves, points out its value in extending our knowledge of the whole process of wave propagation in dispersive media. The corresponding problem for shallow-water waves has an added interest in this connexion, as it illustrates the case, not yet investigated, where the wave-velocity and group-velocity are finite for all wave-lengths, this being the case most frequently met with in optics‡. This paper is also intended especially to illustrate the extended application of the principle of stationary phase outlined in a recent paper §.

According to Fourier's theorem the displacement, ξ , at any point of the free surface at time t , arising from an initial elevation confined to the immediate neighbourhood of the origin, is expressed by

$$\xi = \frac{1}{\pi} \int_0^x dk \cos kx \cos \sigma t, \text{ where } \sigma = kV = (gk \tanh kh)^{1/2}. \quad (1)$$

In the above, h represents the uniform depth of the fluid,

* Communicated by the Author.

† Proc. Roy. Soc. vol. lxxxiii. p. 347 (1910).

‡ Phil. Mag. vol. xxxix. pp. 653-659 (June 1920).

§ Phil. Mag. vol. xlv. pp. 1156-1167 (June 1923).

and V represents the wave-velocity corresponding to wavelength $\frac{2\pi}{k}$. As stated by Lord Rayleigh, the difficulty in the evaluation of the integral lies in the fact that, as written above, it is divergent. Similarly, in the equivalent expression,

$$\xi = \frac{1}{2\pi} \int_0^\infty dk \cos(kx - \sigma t) + \frac{1}{2\pi} \int_0^\infty dk \cos(kx + \sigma t), \quad (2)$$

both integrals are divergent; but these integrals can each be transformed into two integrals, one of which is divergent and the other convergent, by the method indicated in the equation

$$\begin{aligned} \int_0^\infty dk \cos(kx - \sigma t) &= \frac{1}{x} \int_0^\infty dk \left(x - \frac{d\sigma}{dk} t \right) \cos(kx - \sigma t) \\ &+ t \int_0^\infty dk \frac{d\sigma}{dk} \cos(kx - \sigma t). \quad \dots \quad (3) \end{aligned}$$

If in the first term on the right we put $k'x = kx - \sigma t$, the integral becomes $\int_0^\infty dk' \cos k'x$, which, according to Fourier's integral theorem, represents a quantity which is zero at all points except at $x=0$. We can accordingly evaluate ξ from the expression

$$\begin{aligned} \xi &= \frac{t}{2\pi x} \left[\int_0^\infty dk \frac{d\sigma}{dk} \cos(kx - \sigma t) - \int_0^\infty dk \frac{d\sigma}{dk} \cos(kx + \sigma t) \right] \\ &= \frac{t}{\pi x} \int_0^\infty dk \frac{d\sigma}{dk} \sin kx \sin \sigma t, \quad \dots \quad (4) \end{aligned}$$

provided we exclude the origin. The integrals obtained in (4) are in general convergent.

The application of (4) to the case of infinitely deep water ($\sigma^2 = gk$) gives

$$\begin{aligned} \xi &= \frac{g^{1/2} t}{4\pi x} \left[\int_0^\infty dk k^{-1/2} \cos(kx - \sigma t) \right. \\ &\quad \left. - \int_0^\infty dk k^{-1/2} \cos(kx + \sigma t) \right], \quad \dots \quad (5) \end{aligned}$$

by Pidduck. Its first term is given by

$$\begin{aligned} T_1 &= \frac{gt^2}{2\pi x} \left[\int_0^\infty dk \tanh kh \sin kx + h \frac{d}{dh} \int_0^\infty dk \tanh kh \sin kx \right] \\ &= \frac{gt^2}{2\pi x} \left[\left(1 + h \frac{d}{dh} \right) \left(\frac{\pi}{2h} \operatorname{cosech} \frac{\pi x}{2h} \right) \right] \\ &= \frac{gt^2 \pi}{8h^2} \cosh \left(\frac{\pi x}{2h} \right) / \sinh^2 \left(\frac{\pi x}{2h} \right). \quad \dots \dots \dots (9) \end{aligned}$$

The second term is given by

$$\begin{aligned} T_2 &= \frac{2!}{4!} g^2 t^2 \frac{dT_1}{dh} \\ &= -\frac{g^2 t^4 \pi}{384 h^4} \left\{ 4h \sinh \frac{\pi x}{h} - \pi x \left(3 + \cosh \frac{\pi x}{h} \right) \right\} / \sinh^3 \frac{\pi x}{2h}. \quad \dots \dots \dots (10) \end{aligned}$$

These values for the first two terms of the series are given by Pidduck. All the higher order terms in succession can be obtained from these by means of the equation

$$T_n = -\frac{(2n-4)!}{2n!} g^2 t^4 \frac{dT_{n-2}}{dx^2} + \frac{1}{(n-1)!} \cdot \frac{(2n-2)!}{2n!} g t^2 \frac{dT_{n-1}}{dh}. \quad \dots \dots \dots (11)$$

In this way it is easy to derive the terms, but as the series converges very slowly at first and is only suitable for calculation when t is small, it is unnecessary to give the terms in full.

The values of the first six terms of the series, corresponding to the conditions $t = 1$ second and $h = 2$ feet, are shown in the accompanying table for values of x from

x .	T_1 .	T_2 .	T_3 .	T_4 .	T_5 .	T_6 .	ξ .
4	·272	·413	·764	·171	+·102	-·050	·15
5	·124	·318	·311	-·024	+·073	-·019	·162
6	·056	·204	·104	-·058	+·039	-·005	·135
7	·026	·120	·016	-·045	+·015	+·0001	·100
8	·012	·067	+·0119	-·027	+·0046	+·0011	·069
9	·0054	·036	+·0164	-·014	+·0003	+·0009	·045
10	·0024	·019	+·0136	-·0062	-·0009	+·00057	·028

4 to 10. In the calculation of these terms the approximate expressions for the successive terms, indicated by

$$T_1 = \frac{gt^2 \pi}{4h^2} e^{-\frac{\pi x}{2h}} \quad \dots \dots \dots (12)$$

for the first term, have been employed. The approximation is very close from $x = 5$ onwards, and at $x = 4$ the error in the value obtained for ξ arising from the use of the approximate expressions is about four per cent. To obtain the value of ξ at time $t = 1$ second corresponding to any value of x less than 4 we should require to use the exact values of the terms. The series indicated above, with the numerical values of the terms given in the table, would be useful for all values of t less than unity, but the labour involved in calculating the value of ξ by means of the above series when t exceeds unity would be much too great. We shall now show that the calculation can be carried out much more simply for all values of t greater than unity by an entirely different method, depending on the principle of stationary phase treated in my former paper*.

In the expression (2), the displacement ξ appears as the resultant effect due to two systems of wave-trains moving in opposite directions. In considering the displacement at any point for which x is positive we may take

$$\xi = \frac{1}{2\pi} \int_0^{\infty} dk \cos(kx - \sigma t), \quad \sigma = (gk \tanh kh)^{1/2}, \quad (13)$$

in which only positive values of k are considered. The omitted integral we shall deal with later on. This integral in (13) is similar to that discussed in the paper above referred to. At any point x at time t the phase-curve is a curve with two stationary points, one at a positive and one at a negative value of k , and the point of inflexion is at $k=0$. At any time t the points of stationary phase for all points near the front of the wave-system correspond to very small values of k , and an exceedingly close approximation to the true value of ξ is then given by

$$\xi = \frac{1}{2\pi} \int_0^{\infty} dk \cos \left[k(x - \sqrt{gh}t) + \frac{k^3}{6} \sqrt{gh^3}t \right] \quad (14)$$

or by

$$\xi = \frac{1}{2\pi} \cdot \left(\frac{3\pi}{\sqrt{gh^3}t} \right)^{1/3} \int_0^{\infty} dz \cos \frac{\pi}{2} (z^3 - mz), \quad (15)$$

where

$$m = \frac{2}{\pi} \left(\frac{3\pi}{\sqrt{gh^3}t} \right)^{1/3} (\sqrt{gh}t - x).$$

The value of the above integral, for positive or negative

* Phil. Mag. (June 1923).

values of m , has been obtained in terms of the Bessel's Functions, $J_{1/3} \left\{ \pi \binom{m}{3}^{3/2} \right\}$ and $J_{-1/3} \left\{ \pi \binom{m}{3}^{3/2} \right\}$. Numerical values have also been given by Airy for the range $m = -5.6$ to $+5.6$. The above evaluation is valid for all negative values of m and for positive values subject to the condition that

$$k_1^2 = \frac{2(\sqrt{gh}t - x)}{\sqrt{gh^3}t} = \text{a very small quantity,} \quad (16)$$

k_1 being the value of k positive for which the phase is stationary at point x at time t . This condition excludes all values of x small compared with $\sqrt{gh}t$, and it also excludes large values of m unless t also is very large compared with $(\sqrt{gh}t - x)$. In the immediate neighbourhood of the point $x = \sqrt{gh}t$ the above is valid over a very large range of t . At $t = 1$ second, $x = 8$, the above integral gives for ξ the value .070 as against .069 obtained by the previous calculation by means of the series. The limitation expressed by (16) above renders the expression (14) invalid for values of k greater than about .1 in the case of a wave-disturbance in shallow water. But (14) is of considerable importance in relation to dispersion in general. It represents a wave-disturbance advancing in any medium which is only slightly dispersive, being applicable to all substances to which Cauchy's law of dispersion applies*.

The principle of stationary phase may be applied to evaluate (13) without the limitation referred to above. The true phase curve for (13) may be written in the form

$$\phi(k) = \sqrt{\frac{g}{h}} \cdot t \cdot z \left(\alpha - \frac{\tanh^{1/2} z}{z^{1/2}} \right), \text{ where } z = kh \quad (17)$$

and α represents $x/(\sqrt{gh}t)$. We then have

$$\begin{aligned} \frac{d\phi}{dk} &= \sqrt{gh} \cdot t \left\{ \alpha - \frac{1}{2} \frac{\tanh^{1/2} z}{z^{1/2}} - \frac{1}{2} \frac{z^{1/2}}{\tanh^{1/2} z} + \frac{1}{2} z^{1/2} \tanh^{3/2} z \right\} \\ &= \sqrt{gh} \cdot t \{ \alpha - F(z) \}, \quad (18) \end{aligned}$$

$$\frac{d^2\phi}{dk^2} = -\sqrt{gh^3} \cdot t \cdot F'(z), \text{ and } \frac{d^3\phi}{dk^3} = -\sqrt{gh^5} t F''(z). \quad (19)$$

The phase curve is only required for positive values of z .

* A diagram of the integral contained in (15) for small values of m is given in a paper on Ship-Waves by Hogner, *Arkiv för Matematik, Astronomi och Fysik*, Band xvii. No. 12 (1923).

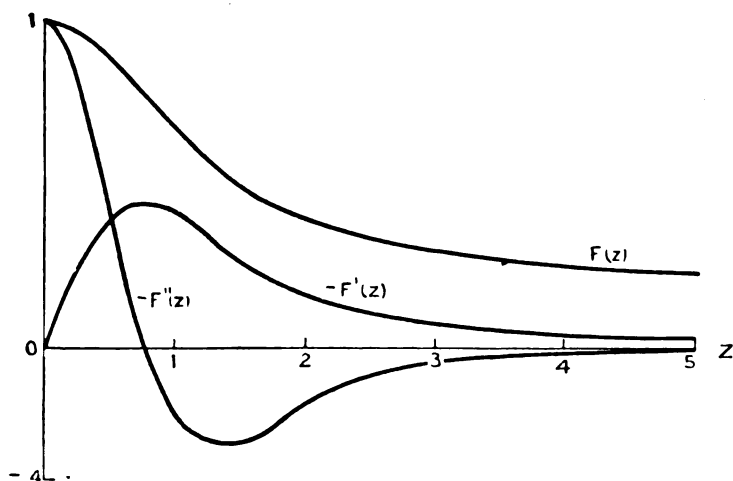
It has a point of inflexion at the origin and a zero at the point defined by $\alpha^2 = \tanh z/z$, provided α is less than unity. Between the origin and this point, at k_0 say, there is a point of stationary phase at which $\alpha = F(z)$. The method to be used in the evaluation of ξ consists in replacing the true phase curve by an auxiliary phase curve, which is in close agreement with the true phase curve at the point k_0 , and for a range on either side of k_0 . In the notation employed in my former paper, the auxiliary phase curve, at point x at time t , is that represented by

$$\phi_1 = a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3, \quad \dots \quad (20)$$

where $a = \phi(k_0)$, $b = \phi''(k_0)$, $c = \phi'''(k_0)$, and $\sigma = (k - k_0)$.

For values of z exceeding $z=4$, $\tanh z=1$, and the phase curve practically coincides with the phase curve for the case of infinitely deep water. This range of values of z or $k_0 h$ corresponds with small values in α or $x/(\sqrt{gh}t)$ and for these values of x and t the displacement curve is nearly the same for infinitely deep water and for shallow water of any assigned depth. As the displacement in infinitely deep water corresponding to our initial displacement is fully

Fig. 1.



determined by the investigations of Professor Lamb, we require to investigate the displacement corresponding to the range of values of z from zero to four.

In figure 1 the diagrams represent $F(z)$, $-F'(z)$, and $-F''(z)$ respectively so that the values of b and c required

in (20) can be read direct from these curves with the correct sign indicated by the diagram. The method of using these curves is as follows:—For any assigned α find z_0 to fulfil the condition $\alpha = F(z_0)$, then with this value of z in (17) calculate $\phi(k_0)$ or a , and with the same value of z find b and c from the curves in figure 1. From the values of a, b, c , so found, the auxiliary phase curve at x at time t is determined. The auxiliary phase curve determined in this way varies in type for different values of z . Thus for any value of z from zero to $\cdot 76$, b and c are both positive and the general shape of the curve is similar to that of the true phase curve over the full range of k from 0 to x . In this range of z , therefore, the auxiliary curve can be employed for integration over the full range of k from 0 to ∞ . For example, with

$$x/(\sqrt{gh}t) = \cdot 875, \quad h=2, \quad t=1, \quad z_0 = k_0 h = \cdot 53, \quad a = -\cdot 0435 \sqrt{\frac{g}{h}} t$$

$$b = \cdot 401 \sqrt{gh^3} t, \quad c = \cdot 350 \sqrt{gh^5} t, \text{ and}$$

$$\xi = \frac{1}{2\pi} \int_{-k_0}^{\infty} d\sigma \cos \left\{ a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3 \right\}. \quad (21)$$

If we transfer the origin to the point of inflexion on the auxiliary phase curve, by the substitution $w = \left(\frac{c}{3\pi} \right)^{1/3} \left(\sigma + \frac{b}{c} \right)$, the above expression becomes

$$\xi = \frac{1}{2\pi} \left(\frac{3\pi}{c} \right)^{1/3} \int_{\rho}^{\infty} dw \cos \left\{ \left(a + \frac{1}{3} \frac{b^3}{c^2} \right) + \frac{\pi}{2} (w^3 - mw) \right\}, \quad (22)$$

where $\rho = \left(\frac{c}{3\pi} \right)^{1/3} \left(\frac{b}{c} - k_0 \right)$, and $\pi \left(\frac{m}{3} \right)^{3/2} = \frac{1}{3} \frac{b^3}{c^2}$. The integrals

$$\int_0^{\infty} dw \cos \left\{ \frac{\pi}{2} (w^3 - mw) \right\} \quad \text{and} \quad \int_0^{\infty} dw \sin \left\{ \frac{\pi}{2} (w^3 - mw) \right\}$$

have been evaluated in the paper already referred to, and the integrals

$$\int_0^{\rho} dw \cos \left\{ \frac{\pi}{2} (w^3 - mw) \right\} \quad \text{and} \quad \int_0^{\rho} dw \sin \left\{ \frac{\pi}{2} (w^3 - mw) \right\}$$

are easily evaluated by quadratures for small values of ρ . In this way, at $t=1$ second, $x=7$, the value obtained for ξ is $\cdot 101$ as against $\cdot 100$, the value given by the convergent series in the table on page 186, thus proving that the above evaluation is valid up to $z = \cdot 53$ from $z=0$.

In the neighbourhood of $z = .76$ the type of the auxiliary curve changes owing to the vanishing of c . Thus, with

$$x/(\sqrt{gh}t) = .75, \quad z_0 = k_0 h = .83, \quad a = -.1295 \sqrt{\frac{g}{h}} t,$$

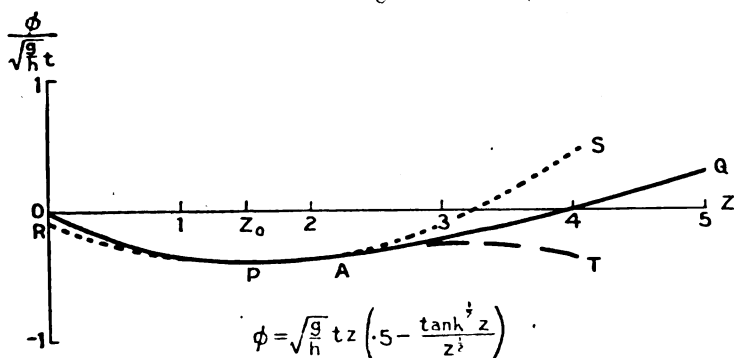
$b = .436 \sqrt{gh^3} t$, $c = a$ a very small negative quantity.

Since c is negative, the auxiliary phase curve (20) differs in type from the true phase curve beyond the point of inflexion on the auxiliary curve, which, therefore, cannot be used to replace the true phase curve over the full range of k . As c is small, however, a very close approximation to the value of the displacement is given by

$$\begin{aligned} \xi &= \frac{1}{2\pi} \int_{-k_0}^{\infty} d\sigma \cos \left\{ a + \frac{b\sigma^2}{2!} \right\} \\ &= \frac{1}{2(\frac{b}{2\pi})^{1/2}} \cos \left(a + \frac{\pi}{4} \right) + \frac{1}{(2\pi^2 b)^{1/2}} \left\{ \cos a \int_0^{(\frac{b}{2})^{1/2} k_0} dy \cos y^2 \right. \\ &\quad \left. - \sin a \int_0^{(\frac{b}{2})^{1/2} k_0} dy \sin y^2 \right\}. \quad (23) \end{aligned}$$

The integrals in this case are well known, and the result is valid over a large area of t . At $t = 1$ second, (23) gives $\xi = .134$, as against $.135$ as given in the table on page 186.

Fig. 2.



If we now take $x/\sqrt{gh}t = .5$, we have $z_0 = k_0 h = 1.522$, $a = -.414 \sqrt{\frac{g}{h}} t$, $b = .266 \sqrt{gh^3} t$, $c = -.3 \sqrt{gh^3} t$. The auxiliary phase curve given by (20) is a cubic, which agrees closely with the true phase curve near the point of stationary phase P, but differs from it in type beyond the point of inflexion A.

It is clear from the diagram of figure 2, in which OPQ represents the true phase curve, that no single curve can

replace the true phase curve over its full range. Over the finite range from $z=0$ to $z_0=1.522$, it is best to employ the true phase curve itself, though a fairly accurate result is

obtained by replacing it by a sine curve, $a \sin \frac{\pi z}{2z_0}$. Thus, for this portion of the curve the integration along the true phase curve leads to the result $\xi_1 = \frac{.278}{2\pi}$ or .044. For the range from $z_0=1.522$, the stationary phase point, to $z=\infty$ we might employ the auxiliary phase curve $\phi = \left(a + \frac{b\sigma^2}{2}\right)$. This gives us

$$\xi_2 = \frac{1}{2\pi} \int_0^\infty d\sigma \cos\left(a + \frac{b}{2}\sigma^2\right), \quad . \quad . \quad . \quad (24)$$

and at $t=1$ the value obtained for ξ_2 is +.062, and with $\xi = \xi_1 + \xi_2$, ξ is .106. According to our former calculation ξ is .15, so that in this case the auxiliary curve employed does not give a sufficiently close approximation at $t=1$. The above auxiliary curve, represented in the diagram by the dotted line RPS, is moderately close to the true phase curve in the range from $z=0$ to $z=3$, or even 4, but, as the diagram shows, it is not in sufficiently good agreement with the true phase curve beyond $z=4$. Another approximate value is obtained if we employ this dotted curve in the range $z=0$ to $z=4$, thus giving

$$\xi_1 = \frac{1}{2\pi h} \int_{-z_c}^{4-z_0} dz \cos\left(a + \frac{b}{2h^2}z^2\right), \quad . \quad . \quad . \quad (25)$$

in which the origin of z is at the point of stationary phase P. In the range from $z=4$ to $z=\infty$ we may take

$$\xi_2 = \frac{1}{2\pi h} \int_4^\infty dz \cos\left[\sqrt{\frac{g}{h}} \cdot t(z\alpha - z^2)\right], \quad . \quad . \quad (26)$$

which is identical with the corresponding integral for the case of infinitely deep water, being obtained from (13) by putting $\tanh kh = \tanh z = 1$. By means of the substitution

$y^2 = \sqrt{\frac{g}{h}} \cdot t\alpha \left(z^2 - \frac{1}{2\alpha}\right)^2$, we can transform the expression (26) into

$$\begin{aligned} \xi_2 = & -\frac{1}{2\pi h} \frac{1}{\sqrt{\frac{g}{h}} \cdot t\alpha} \sin\left(\kappa^2 - \sqrt{\frac{g}{h}} \frac{t}{4\alpha}\right) \\ & + \frac{1}{2\pi h} \cdot \frac{2}{\left(\sqrt{\frac{g}{h}} \cdot t\alpha\right)^{1/2}} \cdot \int_\kappa^\infty dy \cos\left\{y^2 - \sqrt{\frac{g}{h}} \frac{t}{4\alpha}\right\}, \quad (27) \end{aligned}$$

where $\kappa^2 = \sqrt{\frac{g}{h}} \cdot t\alpha \left(4^{1/2} - \frac{1}{2\alpha} \right)$. Corresponding to

$$\alpha = \frac{x}{\sqrt{gh} \cdot t} = .5, \quad h=2, \quad t=1,$$

we obtain $\xi_1 = .128$, $\xi_2 = .007$, and $\xi = .135$ instead of .15 as given by our former calculation. The discrepancy remaining in the results given by the two different methods is due to the fact that even in the range $z=0$ to $z=4$ the auxiliary phase curve indicated by the dotted line is not sufficiently close to the true phase curve: and the above calculations are given to indicate the limitations to the use of the method of stationary phase in certain cases. The auxiliary phase curve,

$$\phi = a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3 = a + \frac{b}{2h^2} (z-z_0)^2 + \frac{c}{6h^3} (z-z_0)^3,$$

is, as is to be expected, better than the dotted curve, being almost in exact agreement with the true phase curve over the range from $z=0$ to $z-z_0 = -\frac{b}{c}$, the point of inflexion on the auxiliary curve; that is, from $z=0$ to $z=2.412$ in the present case ($\alpha=.5$). For this range we have

$$\xi_1 = \frac{1}{2\pi h} \int_0^{z_0 - \frac{b}{c}} dz \cos \left\{ a + \frac{b}{2h^2} (z-z_0)^2 + \frac{c}{6h^3} (z-z_0)^3 \right\},$$

$$z_0 - \frac{b}{c} = 2.412, \quad . \quad . \quad . \quad . \quad (28)$$

as a very close approximation to the correct value of the integral. For the range from $z=2.412$, the best result obtainable by means of an auxiliary curve is given by

$$\xi_2 = \frac{1}{2\pi h} \int_{z_0 - \frac{b}{c}}^{\infty} dz \cos \left[\sqrt{\frac{g}{h}} \cdot t(z\alpha - z^{1/2}) \right]. \quad (29)$$

The auxiliary curve employed in this agrees closely with the true curve in the range $z > 4$, but gradually falls below it in the range from $z=4$ to $z=2.412$. The numerical results at $t=1$ are here $\xi_1 = .047$, $\xi_2 = .093$, and $\xi = .140$. By employing the true phase curve in the range from $z=2.412$ to $z=4$, the value obtained is $\xi = .143$, which is in fair agreement with the result given by the series in the table on page 186 namely, $\xi = .15$. As stated earlier, the value given by the series may, in this case, be inaccurate to four or five per cent.,

and, in addition, the second integral in (2) has still to be added to the value obtained above, as its value increases as α diminishes, and at $\alpha = .5$ it is no longer negligible.

When we proceed to values of $x/\sqrt{gh}.t$ less than $.5$, the point of stationary phase P moves further and further from the origin. For the portion of the true phase curve from z_0 to ∞ , the value of ξ_2 given by (29) approximates closer to the true value of the integral as z_0 increases. The portion of the true phase curve OP is represented very closely by the cubic (20) as far as $\alpha = .4$, which corresponds with the value $z_0 = 2$. But for $z_0 > 2$ the cubic tends to fall below the true phase curve, and it ceases to give a sufficiently close approximation to the value of the integral for the portion OP of the true phase curve. When $\alpha < .4$, $z_0 > 2$, the true phase curve OP lies between the curves $\phi = a \sin \frac{\pi z}{2 z_0}$, and $\phi = \sqrt{\frac{g}{h}}(z\alpha - z^{1.2})$,

for both of which the integrals can be evaluated. It agrees closely with the latter curve when z_0 is considerably larger than 4, and the whole phase curve then is nearly identical with the corresponding curve for infinitely deep water. A cubic auxiliary phase curve which is in fairly good agreement with the true phase curve over range OP can always be obtained by taking a and b to fit the true phase curve at P as formerly, and by then choosing c so that the auxiliary curve passes through the origin. This method requires the values of the integrals

$$\int_0^A dw \cos \frac{\pi}{2}(w^3 - mw) \quad \text{and} \quad \int_0^A dw \sin \frac{\pi}{2}(w^3 - mw)$$

for all values of m and A , and these can be obtained readily by means of results given in a former paper provided

$$\int_0^A dw \cos \frac{\pi}{2} w^3 \quad \text{and} \quad \int_0^A dw \sin \frac{\pi}{2} w^3$$

are first determined. But the work of preparing the numerical values required for the convenient application of the stationary phase method to the evaluation of any integral must meantime be reserved for a later paper.

In the present paper we have proved by means of the evaluations given above, corresponding to $t=1$, that the method of stationary phase can be applied to integrals of the type (13) without the restriction to large values of t contained in former applications. All the evaluations of ξ given above, corresponding to various values of α , are valid for all

values of t ; and it is possible, therefore, by this method to trace the development of the wave-system as time advances. The effect of an increase in t can be most readily determined by writing the phase ϕ in the form

$$\phi = [k\{x - Vt\}] = t \left\{ k \frac{dkV}{dk_0} - kV \right\}.$$

In this we are treating $\frac{x}{t}$ as a constant, corresponding to the α employed above, x being the point at which the phase is stationary for wave-length $2\pi/k_0$. When we express ϕ , the true phase, in a series of terms depending on σ or $(k - k_0)$, it now takes the form

$$\phi = t \left\{ \alpha_0 + \frac{\beta_0}{2!} \sigma^2 - \frac{\gamma_0}{3!} \sigma^3 + \text{etc.} \right\}$$

instead of

$$\phi = a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3 + \text{etc.},$$

as given in my former paper*.

From this it appears that if we take the true phase curve and the corresponding auxiliary phase curve at $t=1$, we have to increase the ordinates of each of these curves in the same ratio ($t/1$) to obtain the true phase curve and auxiliary phase curve at any later time t . The fit of the curves giving the correct result and the approximate result respectively is not altered as t increases. This does not necessarily prove that the approximation to the true value of the integral obtained by means of the auxiliary curve is equally good for all values of t . A test would need to be made in each individual case to prove this. Thus, in the case where the true phase curve is given by $\phi = t\{\beta\sigma^2 + \gamma\sigma^3\}$ and the auxiliary phase curve is given by $\phi = t\{\beta\sigma^2\}$, it is easy to show that the integral

$$\int_0^\infty d\sigma \cos\{t(\beta\sigma^2 + \gamma\sigma^3)\}$$

is represented with fair accuracy by

$$\int_0^\infty d\sigma \cos\{t\beta\sigma^2\}$$

when t is large, and the accuracy of the

approximate value improves as t becomes larger. We have, in fact, the approximate evaluation, for β and γ positive,

$$I = \int_0^\infty d\sigma \cos\{t(\beta\sigma^2 + \gamma\sigma^3)\} = \frac{1}{2} \sqrt{\frac{\pi}{2\beta t}} \left\{ 1 - \frac{5.3.1}{2^3.2!} \frac{\gamma^2}{\beta^2 t} \right\},$$

the approximate evaluation being given by the first term

* Phil. Mag. xlv. pp. 1156-1167, June 1923.

alone. The above example indicates the reason why t must be taken large in Lord Kelvin's original applications of the principle of stationary phase.

In the evaluations of the integral (13) we have confined our attention to the range of x and t for which the phase curve has a stationary point. At time $t=1$ a stationary point exists on the phase curve for all values of x from 0 to 8. From $x=8$ to $x=\infty$ the phase curve has no stationary point. It is then of the same type as the phase curve $\phi=kx+\sigma t$, which appears in the second integral in equation (2) and which we have treated as negligible throughout. The corresponding integrals represent a disturbance which diminishes rapidly towards zero as x increases, of the type indicated by the advanced portion of the curve shown in

Fig. 3.

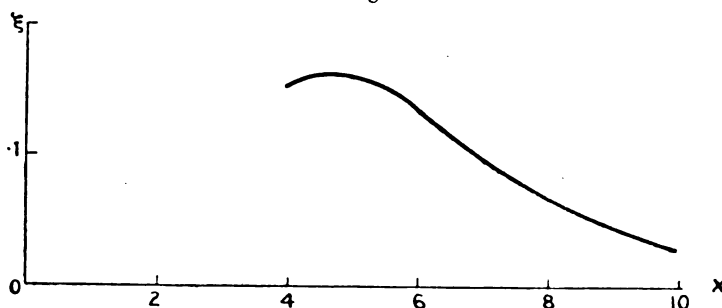


figure 3, which represents the displacement curve at $t=1$ in the range from $x=4$ to $x=10$ to which our calculations refer. These integrals can be evaluated by the method employed above, in which the true phase curve is replaced by an auxiliary curve, but for this evaluation the integrals referred to on page 194 above are again required.

The following table gives the numerical values from which the curves in figure 1 are obtained:—

z .	$F(z)$.	$-F''(z)$.	$-F'''(z)$.
0.0	1.000	.000	1.000
.25	.970	.234	.814
.5	.890	.388	.404
.75	.784	.439	.02
1.0	.676	.411	-.212
1.5	.506	.273	-.301
2.0	.398	.161	-.173
3.0	.296	.063	-.049
4.0	.250	.034	-.016

XVII. *Bending Stresses in Thin-Walled Tubes.*

By JOHN CASE, M.A., F.R.Ae.S.*

1. *Summary and Conclusions.*

THE object of the present paper is the investigation of the stresses in a thin tubular beam, such as steel factory chimneys, monocoque fuselages of aeroplanes, the hulls of submarine vessels, and the like. Beams such as these are liable to fail at a smaller load than is that calculated by the simple theory of bending, and, so far as the author is aware, no method of calculating the strength in these cases has been given before. The method developed here is perfectly general in principle, and can be applied to thin tubular beams of any cross-section, such as submarine hulls or steel spars for aeroplanes.

Considering, first, beams of circular cross-section, it is shown below that any section of the beam behaves as a ring under an external radial pressure which varies from point to point of the circumference. On account of this pressure a ring such as ABC (fig. 1), of unit axial length, is subjected to a maximum bending moment

$$m = \frac{M^2 r^3 t}{4 EI^2},$$

where M is the bending moment applied to the beam, r is the mean radius of the cross-section, t is the thickness of the walls of the tube, I the moment of inertia of the cross-section, and E is Young's Modulus. This bending moment acts in the plane of the cross-section, and gives rise to a stress

$$\frac{3 M^2 r^3}{2 EI^2 t} = \frac{3 M^2}{2 \pi^2 E r^3 t^2}$$

at the points of the section which are in the principal plane of bending and points separated from these by 90° .

It will be seen that this stress, which is of opposite sign on the outer and inner surfaces of the tube, increases as the square of the applied couple, and inversely as the cube of the diameter and the square of the thickness of the cross-section.

It is shown below that this circumferential stress will exceed the longitudinal stress f if

$$\frac{r}{t} > \frac{E}{6f}.$$

* Communicated by the Author.

If we take f as the yield point of the material, and the maximum stress as the criterion of breakdown, this means that in the case of a steel having a yield point of 50,000 lb./in.², the circumferential stress will cause failure if the diameter of the tube is 800 times the thickness. If the maximum stress difference is the criterion, the circumferential stress will become important for a smaller diameter of tube, since at some points in the section it will give rise to a compressive stress at right angles to a longitudinal tensile stress and *vice versa*. Thus, if the diameter is 400 times the thickness, the bending moment which the tube can stand is reduced by 15 per cent.

These figures will show that the circumferential stresses only become important when the ratio thickness/diameter is very small; I am of opinion that in these cases it is the circumferential stresses which bring about the so-called buckling of the tube.

A similar expression to the above is given for an elliptic tube in equation (22) below, and the equations for any symmetrical section are given in (24) and (25). In the case of the hull of a submarine vessel, every cross-section is subjected to hydrostatic pressure as well as the pressure arising from flexure. If the hydrostatic pressure be written in the form $a - by$, where a and b are constants and y is the height of a point above the axis of the ship, which is here supposed to be of circular section, the circumferential stress is given by

$$\frac{3 M^2 r^3}{2 EI^2 t} \cos 2\theta + \frac{6br^3}{t^2} \left[\frac{2}{\pi} + \left(\frac{\theta}{\pi} - \frac{\pi}{4} \right) \cos \theta - \frac{\sin \theta}{2} \right],$$

where θ is measured from a horizontal diameter and the other letters have the same meaning as above.

Asymmetrical sections can be dealt with on the same principles as symmetrical sections, if due consideration is given to the distortion.

2. Beams of Circular Section (figs. 1 & 2).

Fig. 1.

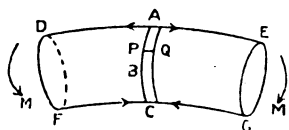


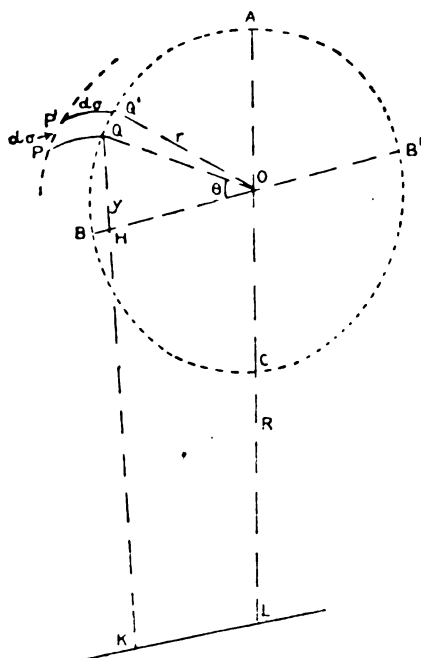
Fig. 2.



The beam is supposed under the action of couples M only.

The longitudinal fibres on the convex side DE are in tension and those on the concave side FG are in compression. Consider the ring ABC , and let PQ be an element of the top part of this ring, parallel to the plane of bending. This element will be acted on by forces of intensity T per unit area, exerted by the neighbouring rings, T being the stress intensity due to bending. Similar considerations will apply all round the ring. Thus, if we imagine the tube made up of a number of rings, each ring will be under the action of a radial pressure on account of the adjoining rings. This pressure will give rise to circumferential stresses in the ring.

Fig. 3.



We shall assume that each ring behaves as if it were entirely independent and acted upon by a radial pressure equivalent to the normal components of the stresses T .

In fig. 3, AOC is a diameter of one boundary of the ring, and lies in the plane of bending; BOB' is a diameter perpendicular to this.

KL is the intersection of the planes containing the boundaries of the ring, so that OL is the radius of the circle into which the centre line of the tube bends.

PP'Q'Q is an element of the ring, PQ and P'Q' being lines which before strain were parallel to the axis of the tube.

N is the intersection of the normals to the surface at P and Q (QON is a continuation of the radius QO).

Let $OL = R$,

$OQ = r$,

$QH = y$,

$PQ = d\sigma$,

$PP' = ds$,

$QK = \rho$,

$QKP = \phi$,

$QOH = \theta$,

T = tensile stress across PP' and QQ' ,

t = the thickness of the walls of the tube.

Then the total force on PP' and QQ' is $Tt \cdot ds$.

The radial pressure on the element due to these is

$$2Tt \, ds \cdot \frac{d\phi}{2} = Tt \, ds \cdot d\phi.$$

The area of $PP'Q'Q$ is $ds \cdot d\sigma$.

Hence the equivalent radial pressure on $PP'Q'Q$ is

$$p = \frac{Tt \cdot ds \cdot d\phi}{ds \cdot d\sigma} = Tt \frac{d\phi}{d\sigma} = \frac{Tt}{\rho} \quad \dots \quad (1)$$

Also

$$\rho = R + y = R + r \sin \theta. \quad \dots \quad (2)$$

Assume that T is still given with sufficient accuracy by the usual formulæ, so that

$$T = \frac{My}{I} = \frac{Mr \sin \theta}{I}, \quad \dots \quad (3)$$

where I is the moment of inertia of the section of the tube about BB' .

Hence, from (1), (2), and (3),

$$p = \frac{Mrt \sin \theta}{I(R + r \sin \theta)}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

but

$$\frac{1}{R} = \frac{M}{EI},$$

where E is Young's Modulus.

Hence

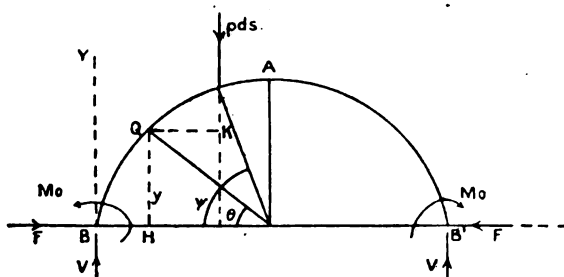
$$p = \frac{M^2 r t}{EI^2} \cdot \frac{\sin \theta}{1 + \frac{r}{B} \sin \theta}.$$

Let us neglect r/R in comparison with unity, then

$$p = \frac{M^2 r t}{EI^2} \sin \theta. \quad (5)$$

Consider, then, a ring of unit width subject to this radial pressure.

Fig. 4.



The action of the lower half on the upper can be represented by a bending moment M_0 , a tension V , and a shearing force F , as shown in fig. 4, at B and B'. Take B as origin, and measure x to the right.

By symmetry $F=0$.

Let m = bending moment at Q.

Then

$$\begin{aligned}
 m &= \int_Q^{B'} p ds \cdot QK - V \cdot HB' + M_0 \\
 &= \int_\theta^\pi p r^2 (\cos \theta - \cos \psi) d\psi - V r (1 + \cos \theta) + M_0 \\
 &= \frac{M^2 r^3 t}{EI^2} \int_\theta^\pi \sin \psi \cdot (\cos \theta - \cos \psi) d\psi - V r (1 + \cos \theta) + 0.
 \end{aligned}$$

Also,

$$\begin{aligned}
 V &= \int_0^{\frac{\pi}{2}} p \cdot r d\psi \\
 &= \frac{M^2 r^2 t}{EI^2} \int_0^{\frac{\pi}{2}} \sin \psi \cdot d\psi,
 \end{aligned}$$

which gives

$$V = \frac{M^2 r^2 t}{EI^2} \dots \dots \dots (7)$$

Substituting for (7) in (6) and evaluating the integral leads to

$$\begin{aligned}
 m &= M_0 - \frac{M^2 r^3 t}{4EI^2} (1 - \cos 2\theta) \\
 &= M - \frac{M^2 r^3 t}{2EI^2} \sin^2 \theta \dots \dots \dots (8)
 \end{aligned}$$

By symmetry the total change in the slope of the tangent to the ring between $\theta=0$ and $\theta=\frac{\pi}{2}$, due to deformation, must be zero. Therefore we must have

$$\begin{aligned}
 \int_0^{\frac{\pi}{2}} \frac{mr}{EI} d\theta &= 0, \\
 \text{i. e.} \quad \int_0^{\frac{\pi}{2}} \left(M_0 - \frac{M^2 r^3 t}{2EI^2} \sin^2 \theta \right) d\theta &= 0,
 \end{aligned}$$

since r , E , and I are constant, which gives

$$M_0 = \frac{M^2 r^3 t}{4EI^2}.$$

Hence, from (8),

$$m = \frac{M^2 r^3 t}{4EI^2} \cos 2\theta, \quad \dots \dots \dots (9)$$

m is a maximum when $\theta = 0, \frac{\pi}{2}, \pi$, etc., and is zero when $\theta = \frac{\pi}{4}, \frac{3\pi}{4}$, etc.

The maximum value of m is $\frac{M^2 r^3 t}{4EI^2}$, which gives rise to a circumferential stress in the ring equal to $6m/t^2$, i. e.

$$\frac{3}{2} \frac{M^2 r^3}{EI^2 t} \dots \dots \dots (10)$$

There is also the direct stress in the ring to be considered : the thrust at Q in the direction of the tangent is

$$\int_0^\pi pr \cos \theta d\psi - V \cos \theta,$$

which equals

$$\frac{M^2 r^2 t}{2EI^2} (1 + \cos 2\theta).$$

The corresponding stress is

$$\frac{M^2 r^2}{2EI^2} (1 + \cos 2\theta).$$

When $\theta = 0$ or π , this = $\frac{M^2 r^2}{EI^2}$,

„ $\theta = \frac{\pi}{2}$, the direct stress = zero.

Hence the maximum stress in the ring, due to bending by the action of the radial force, is

$$\begin{aligned} & \frac{3}{2} \frac{M^2 r^3}{EI^2 t} + \frac{M^2 r^2}{EI^2} \\ &= \frac{3}{2} \frac{M^2 r^3}{EI^2 t} \left(1 + \frac{2}{3} \frac{t}{r} \right), \end{aligned}$$

which shows that we can neglect the direct stress.

Next we must consider the shearing force across the edge PQ (fig. 3). Denoting this by S , we see from fig. 4, that

$$S = \int_0^\pi pr \sin \psi d\psi - V \sin \theta.$$

Substituting for p from (5) and performing the integration, this leads to

$$S = \frac{1}{2} \frac{M^2 r^2 t}{EI^2} \sin 2\theta.$$

The cross-section of the ring is a rectangle of width unity and depth t , so that the shear stress is

$$q = \frac{3}{4} \frac{M^2 r^2}{EI^2} \sin 2\theta \quad . \quad . \quad . \quad (11)$$

at a point on the middle surface of the ring, being zero at the outer and inner surfaces.

The bending stress in the ring, due to the radial pressure, is a maximum on the outer and inner surfaces and zero on the middle surface. Also r/t will be large, so that, comparing (10) and (11), we see that we need not consider the shear stress.

Returning now to the element $PP'Q'Q$ of the tube, we see that there is a tensile stress

$$T = \frac{Mr \sin \theta}{I}$$

across the faces PP' and QQ' , and a tensile stress

$$T' = \pm \frac{3}{2} \frac{M^2 r^3}{EI^2 t} \cos 2\theta$$

along the outer and inner edges of the faces PQ and $P'Q'$.

When $\theta=0$ or π , T is zero, and T' is a tensile stress on the outer surface and a compressive stress on the inner surface.

When $\theta = \frac{\pi}{2}$ or $\frac{3\pi}{2}$,

$$T = \frac{Mr}{I} = \frac{M}{\pi r^3 t}, \quad . \quad . \quad . \quad (12)$$

$$T' = \frac{3}{2} \frac{M^2 r^3}{EI^2 t} = \frac{3}{2} \frac{M^2}{\pi^2 E r^3 t^3}, \quad . \quad . \quad . \quad (13)$$

the latter being compressive on the outer surface and tensile on the inner.

Let f be the yield stress of the material, then the bending moment which will cause the longitudinal stress to reach this value is given by

$$f = \frac{M}{\pi r^2 t},$$

i. e.

$$M = \pi r^2 t f.$$

The circumferential or hoop stress will then be (by 13)

$$\frac{3\pi^2 r^4 t^2 f^2}{\pi^2 E r^3 t^3},$$

which equals $\frac{3r}{t} \frac{f^2}{E}$. This will be greater than f if $\frac{3r}{tE} > 1$, i. e. if

$$\frac{r}{t} > \frac{E}{3f} \dots \dots \dots (14)$$

In this case the tube will fail by hoop stress before it fails by longitudinal stress.

In the case of steel, if we take

$$E = 30 \times 10^6, \text{ and } f = 50,000 \text{ lb./in.}^2,$$

this means that the diameter of the tube must be about 800 times the thickness.

In the case of wood with

$$E = 1.5 \times 10^6 \text{ and } f = 5000 \text{ lb./in.}^2$$

the diameter must be about 400 times the thickness.

3. Submarine Hulls.

An extension of the above theory, which is applicable to submarine vessels of circular section, is when the tube is subjected to an external pressure which varies in a linear manner from top to bottom of the tube. In this case we can write:

$$\begin{aligned} p &= a - by + \frac{M^2 r t}{EI^2} \sin^2 \theta \\ &= a - br \sin \theta + \frac{M^2 r t}{EI^2} \sin^2 \theta, \dots \dots \dots (15) \end{aligned}$$

where a and b are constants.

Proceeding in exactly the same way as before, we find

$$V = ar - \frac{\pi r^2 b}{4} + \frac{M^2 r^2 t}{EI^2}, \dots \dots \dots (16)$$

$$M_0 = \frac{M^2 r^3 t}{4EI^2} - \frac{\pi^2 - 8}{4\pi} br^3, \dots \dots \dots (17)$$

$$m = \frac{M^2 r^3 t}{4EI^2} \cos 2\theta + br^3 \left[\frac{2}{\pi} + \left(\frac{\theta}{\pi} - \frac{\pi}{4} \right) \cos \theta - \frac{\sin \theta}{2} \right]. \dots \dots \dots (18)$$

Substituting for $p ds$ in terms of ϕ and integrating from $\phi=0$ to $\phi=\frac{\pi}{2}$, leads to

$$Y = \frac{2M^2a^2t}{3EI^2} \left(1 - \frac{2}{5}e^2\right). \quad (19)$$

Next, let (fig. 5) P be the point $(x_0 = a \cos \phi_0, y_0 = b \sin \phi_0)$ and Q the point $(x = a \cos \phi, y = b \sin \phi)$; also let M_A and M_B be the bending moments at A and B. Then the bending moment at P is given by

$$m = M_A - (a+x)Y + \int_{\phi=\phi_0}^{\phi=\pi} p ds \cdot PZ.$$

Y has been given above, and PZ is given by

$$PZ = (x_0 - x) = a(\cos \phi_0 - \cos \phi)$$

whence we obtain, on substituting and integrating,

$$m = M_A + \frac{M^2a^3t}{EI^2} \left[\frac{7e^2}{24} - \frac{1}{2} + \frac{1}{2} \left(1 - \frac{e^2}{2}\right) \cos^2 \phi_0 - \frac{e^2}{24} \cos^4 \phi_0 \right].$$

As in the case of the circular section, we use the condition $\int_A^B m ds = 0$ to find M_A . The result is

$$M_A = \frac{M^2a^3t}{4EI^2} \left(1 - \frac{23}{48}e^2\right). \quad (20)$$

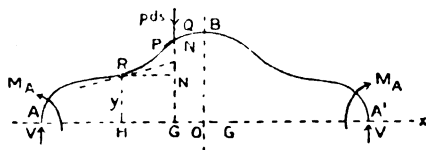
Hence, finally,

$$m = \frac{M^2a^3t}{EI^2} \left[-\left(\frac{1}{4} - \frac{11}{64}e^2\right) + \frac{1}{2} \left(1 - \frac{e^2}{2}\right) \cos^2 \phi - \frac{e^2}{12} \cos^4 \phi \right] \quad (21)$$

from which the stress can be calculated in the same way as before.

5. In the case of irregular sections the integrations must be done graphically by plotting the various curves and finding

Fig. 6.



their areas. Thus, consider the section shown in fig. 6, where there is supposed to be symmetry about both axes.

PQ is an element of arc ds , and then we have

$$p = \frac{M^2 t}{EI^2} \cdot PG$$

$$V = \frac{M^2 t}{EI^2} \int_A^B PG \cdot ds, \quad \dots \dots \dots (22)$$

m = bending moment at R

$$= M_A - HA' \cdot V + \frac{M^2 t}{EI^2} \int_R^{A'} PG \cdot HG \cdot ds, \quad \dots \dots (23)$$

M_A is given by

$$\int_A^B m \, ds = 0,$$

i. e.

$$sM_A = \int_A^B V \cdot HA' \, ds - \frac{M^2 t}{EI^2} \int_A^B \int_R^B PG \cdot HG \cdot ds,$$

where s = the length of the arc AB.

Hence :

$$\begin{aligned} M_A &= \frac{M^2 t}{EI^2 s} \int_A^B \int_A^B (PG \cdot HA' - PG \cdot HG) \, ds \\ &= \frac{M^2 t}{EI^2 s} \int_A^B \int_A^B GA' \cdot PG \cdot ds \quad \dots \dots \dots (24) \end{aligned}$$

The integrals are evaluated by marking off equal intervals of arc along the circumference of the section, measuring GA' and PG , and then plotting the integrands against s .

It is hoped that the method has been sufficiently explained above to enable the reader to deal with any particular case, for the process is not necessarily limited to the symmetrical cases which we have taken. The process should be applicable to such sections as those used for the very thin metal spars of aeroplanes.

When the tube is subjected to shearing forces and direct tensions or thrusts, as well as bending moments, the circumferential stresses due to bending can be found as above, and then the maximum principal stress should be found.

XVIII. *Statistical Equilibrium in relation to the Photo-electric Effect, and its Application to the Determination of Absorption Coefficients.* By E. A. MILNE, *Fellow of Trinity College and Assistant Director of the Solar Physics Observatory, Cambridge* *.

§ 1. *Absorption Coefficients and Probabilities.*

ONE of the desiderata in the physics of the atom is a knowledge of the probability of transitions between different stationary states. Suppose we have an atom in a stationary state which we denote by 1, and that it can also assume another stationary state which we denote by 2. Let the probability that at any instant t the atom will in the succeeding interval dt undergo a transition from state 1 to state 2 be $P_{1 \rightarrow 2} dt$. Here $P_{1 \rightarrow 2}$ is a function of the circumstances of both the states 1 and 2, and also of the environment—that is to say, it may depend in addition on the chances of interference of the atom by another atom during the interval dt and also on the field of radiation to which the atom is subject. We will, however, exclude from consideration the former of these environmental conditions. If the state 1 is of less energy than the state 2, the transition will take place with absorption of radiant energy of a certain frequency ν .

If now the numerical value of $P_{1 \rightarrow 2}$ is known, we can find the absorption coefficient, for frequency ν , of the substance composed of these atoms. For the absorption coefficient is the product of two factors, one proportional to the number of atoms per unit mass capable of absorbing radiation of frequency ν , *i.e.* in the state 1, the other proportional to the probability that any given atom in the state 1 will in fact absorb. The first factor can be found, at least in many cases, from statistical mechanics, and thus the macroscopic absorption coefficient can be calculated if the probability of atomic transition is known.

Conversely, from the measured value of an absorption coefficient the probability of transition can be calculated. Now, in the X-ray region, where the process of absorption gives rise to continuous bands, the absolute values of absorption coefficients are known with accuracy. But in the optical region absorption is for the most part monochromatic, and here the measures are very difficult—hardly

* Communicated by the Director of the Solar Physics Observatory, Cambridge.

any, in fact, exist. Such a measure, for example, in the case of the D lines of sodium, would involve the exact determination of the ratio of the intensity inside the fine absorption line formed by interposing a known thickness of sodium vapour under known conditions in the path of a beam, to the intensity of the corresponding portion of the continuous spectrum of the beam itself.

Wood's measurements* of the absorption of mercury resonance radiation $\lambda 2537$ ($1S-2p_2$) in mercury vapour give values of the mass-absorption coefficient ranging from 0.8×10^9 to 2×10^9 ; for example, a layer of mercury vapour 0.5 mm. thick at 0.001 mm. pressure reduced the intensity of a beam of resonance radiation to $\frac{1}{3}$ of its initial value, a layer 2.5 mm. thick to $\frac{1}{16}$. In view of the values for ordinary X-rays (of the order of 10^9 to 10^2), and of Eddington's value for the material of the interior of a star (of the order of 20-40), such a value appears perhaps astonishingly large, though it is known that vapours are highly absorbent to radiations they themselves emit. Unfortunately, the writer has not been able to find any other experimental data on the subject. But it has been shown from rough considerations arising out of the assumed equilibrium of ionized calcium vapour under selective radiation pressure in the sun's chromosphere† that the mass-absorption coefficient for the H and K lines of calcium should be at least of the order of 10^8 , and probably somewhat greater.

In a similar way, if $P_{2 \rightarrow 1} dt$ is the probability of transition from state 2 to state 1 which occurs with emission of ν -radiation, then $P_{2 \rightarrow 1}$ is connected with the coefficient of emission. It is also connected with the average time of occupancy of an outer orbit by a displaced electron, which is usually denoted by τ . An electron ejected to an outer orbit appears to have a natural tendency to return to the normal orbit, and the average time of existence of the atom in the excited condition has been made the subject of experiment. It appears that τ is of the same order of magnitude, 10^{-8} sec., for the different lines of the different elements that have been investigated‡. Hence $P_{2 \rightarrow 1}$ is of the order of magnitude of 10^8 sec.⁻¹. But it must be noted that the probability $P_{2 \rightarrow 1}$ must be supposed in general to be the sum of two terms, one depending on the intensity of the surrounding radiation, the other depending on the inherent tendency of the electron to return to the state 1.

* Quoted by Foote and Mohler, 'The Origin of Spectra,' p. 89 (1922).

† Fowler and Milne, 'Monthly Notices,' lxxxiii. p. 418 (1923).

‡ Foote and Mohler, *loc. cit.* p. 96.

Bohr's correspondence principle connects the probabilities of transitions between stationary states with the magnitudes of the amplitudes of the corresponding harmonic components in the trigonometrical series which represents the motion. As is well known, it has predicted results of prime importance concerning the relative intensities, for example, in the components of the Stark effect and in the theory of fine structure, but it has not yet provided information as to the absolute values of the probabilities of transitions.

It is, however, the absolute values of the absorption coefficients, and thus of probabilities, that are required in many cases, in particular in the astrophysical investigations out of which the present paper originated. When an absorption line reaches its maximum intensity in the stellar sequence of spectra, it appears to originate in the stellar atmosphere at a depth where the pressure is of the order of 10^{-4} atmos., and the question arises how this may be accounted for on *a priori* grounds. When a detailed theory is constructed, on whatever specific assumptions, the mean pressure for a maximum of intensity in an absorption line is found to depend on the absolute value of the absorption coefficient. In fact, without a detailed calculation, it is clear that the greater the absorbing power of the atoms in question the more opaque is the stellar atmosphere in the frequency concerned, and so the greater the height and the smaller the pressure at which the line originates. From the observed pressure, it is possible on certain assumptions to obtain a relation between the absorption coefficient and certain physical characteristics of the star itself, such as the value of gravity at the surface. Assuming values for the latter, it is possible to obtain estimates of the absolute values of the absorption coefficients of certain spectral lines based entirely on astronomical evidence. Such estimates are in no serious disagreement as regards order of magnitude with the observational value for the H γ line and the value for the H and K lines of Ca deduced by a different line of astrophysical argument. But the estimates are subject to large uncertainties, and it is highly desirable to have them confirmed in any ways that are available.

§ 2. Einstein's Method.

The introduction of probability coefficients such as $P_{1 \rightarrow 2}$ and $P_{2 \rightarrow 1}$ was first made by Einstein* in a classical paper.

* *Verh. d. D. Phys. Gesell.* 1916, p. 318. A more detailed treatment is given in *Phys. Zeit.* xviii. p. 121 (1917).

Einstein considered an enclosure containing a gas whose atoms could assume a number of stationary states, and investigated the equilibrium subsisting between the atoms and the surrounding radiation. He assumed that the transitions between the stationary states were governed by certain definite laws of probability of the kind outlined in § 1 above. Each transition is accompanied by an emission or absorption of radiation, and the totality of transitions must give rise to black body radiation in the enclosure. From this, utilizing the statistical distribution of the atoms amongst the different stationary states, he deduced three results: (1) the quantum formula $h\nu = \Delta W$, for the connexion between frequency and energy change; (2) Planck's formula; (3) a relation equivalent in our notation to one between $P_{1 \rightarrow 2}$ and $P_{2 \rightarrow 1}$. Since the order of magnitude of $P_{2 \rightarrow 1}$ is known from the experimental determination of τ , and since $P_{1 \rightarrow 2}$ determines the coefficient of absorption, the possibility suggests itself of utilizing Einstein's relation to deduce the latter from the former.

The details are given in § 5. It will be found that unfortunately the relation does not yield at present a definite numerical value for $P_{1 \rightarrow 2}$, owing to a fresh unknown quantity which discloses itself, namely, the numerical width of a "monochromatic line."

§ 3. *Scope of the present Paper.*

In an attempt to avoid this difficulty, the author has in § 8 applied Einstein's method to the photo-electric liberation of electrons in a gas at a high temperature, with the production of ionization. An investigation is given of the thermodynamic equilibrium subsisting between atoms, ions, electrons, and radiation in an enclosure at a given temperature*. Just as Einstein's work evaluates the monochromatic absorption coefficients of the various lines of an

* Since this investigation was completed, a paper has appeared by Kramers (Phil. Mag. xlv. p. 836, Nov. 1923) in which Einstein's method is applied to the same problem. Kramers obtains a formula identical with (20) below, though the details of the deduction are different. Kramers' applications are to the absorption and emission of X-rays, i. e. to the inner levels of the atom, whilst the applications of the present paper are to the outer (optical) levels. Space does not permit a detailed comparison. Just as the present paper was being sent to the press, yet another paper on the same subject came to hand, by Becker (*Zeit. für Phys.* xviii. p. 325, 1923). This contains an investigation substantially equivalent to §§ 8-11 of the present paper.

optical series, so the extension to the photo-electric effect evaluates the coefficients of absorption for the continuous spectrum which lies on the short wave-length side of the series limit. Instead of the unknown theoretical breadth of a spectral line, it involves the unknown probability of capture of an electron by an ionized atom. By making definite assumptions about the probability of capture, the coefficient of absorption is evaluated. The result applies in the first instance to the optical region of frequencies. But for a heavily ionized gas at a high temperature this is precisely Eddington's problem of electron-capture in the interior of a star. The formula we obtain can, in fact, be integrated with regard to frequency, so as to give the mean coefficient of absorption of stellar material. The resulting formula agrees with Eddington's, save for a correcting factor which depends on the ionization potentials principally concerned.

§ 4. *General Remarks on Einstein's Method.*

When a case of dissociative equilibrium or any kind of statistical equilibrium is discussed with the aid of a specific kinetic theory, there appears an "equilibrium constant," a function (for any given system) of the temperature only, in the form of a ratio of reaction-velocities. When the equilibrium of the same system is discussed with the aid of thermodynamics, or from probability considerations, the same equilibrium constant appears, but its expression includes no reference to reaction-velocities, for the concept of reaction-velocities is foreign to pure thermodynamics. By confronting the two results, we obtain in general an explicit relation between the reaction-velocities. From thermodynamics alone the reaction-velocities can never be separately determined, but the form of the equilibrium constant imposes a restriction to which all detailed theories of the mechanism of the reactions must conform.

This is the point of Einstein's method. The thermodynamic theory of radiation (Kirchhoff) shows that if ϵ_ν is the coefficient of emission for frequency ν , k_ν the coefficient of absorption, then under equilibrium conditions $\epsilon_\nu/k_\nu = I_\nu$, where I_ν , the intensity of radiation, is a function of temperature only. Einstein's assumptions respecting stationary states and the probabilities of emission and absorption amounted to a detailed theory giving ϵ_ν and k_ν , and his results then followed from the condition $\epsilon_\nu/k_\nu =$ function of temperature, combined with the thermodynamic properties of radiation. The probabilities of emission and absorption

may be regarded as the reaction-velocities of the monomolecular reaction consisting of the transition from one stationary state to another.

It is well known that early attempts at discovering the radiation formula were founded on this method applied in the reverse manner: I_ν was to be found by calculating ϵ_ν and k_ν from some particular atomic model. But familiarity with this instance perhaps obscures the fact that the method is capable of other applications.

The thermodynamic formula first freely used by Saha* for calculating the ionization of a gas at high temperatures is independent of the mechanism of ionization, but it imposes a restriction on any assumed mechanism of ionization and recombination. The mechanism of ionization assumed in § 8 is the photo-electric liberation of electrons; and a relation is found between the probability of ionization of a given atom by radiation and the probability of capture of an electron in a given type of encounter with an ion. But the existence of the thermodynamic state of equilibrium is in no way incompatible with other mechanisms of ionization. Thus ionization may occur by collisions between atoms. This process gives a rate of ionization proportional to the square of the pressure. If the only compensating process were that of the encounter of an ion with an electron, the rate of recombination would be also proportional to the square of the pressure, and therefore the equilibrium constant would be independent of the pressure, in disagreement with the thermodynamic formula and with observation. This shows that there must be some process of recombination other than that of the simple encounter of an ion and an electron. A principle of reversibility† shows that the true compensating process in the case of ionization by collision consists of *three-body encounters* between an ion, an electron, and another atom. The number of such encounters is proportional to the cube of the pressure; hence the ratio of the rates of recombination and ionization is proportional to the pressure simply, just as for ionization by radiation, in agreement with the thermodynamic formula‡.

Considerations of this kind would appear to have an important bearing on some of the vexed questions connected with the theory of monomolecular reactions.

* Phil. Mag. xl. p. 472 (1920).

† Cf. Klein and Rosseland, *Zeit. für Phys.* iv. p. 46 (1921).

‡ The ideas in this paragraph occurred independently and simultaneously to Mr. R. H. Fowler and the writer. See Mr. Fowler's paper on three-body encounters communicated to this Magazine.

§ 5. Application of Einstein's Formula to the Calculation of Monochromatic Absorption Coefficients.

Einstein's argument is as follows. Let 1 and 2 denote two definite stationary states of an atom, and let χ_1 and χ_2 ($\chi_1 > \chi_2$) denote their negative energies. Then the atom will proceed from the state 1 to the state 2 with absorption of radiation of amount $\chi_1 - \chi_2$, and from state 2 to state 1 with emission of the same amount. We assume this radiation to be monochromatic, of frequency ν . Let $A_{2 \rightarrow 1} dt$ be the probability that during the short time dt an atom in the state 2 will of its own accord change to the state 1, with emission of radiation. Einstein calls this "in-radiation." Again, let $B_{2 \rightarrow 1} I_\nu dt$ be the *additional* probability that the same atom will change to the state 1 in time dt under the influence of external isotropic radiation of intensity I_ν . Einstein calls this "out-radiation." Finally, let $B_{1 \rightarrow 2} I_\nu dt$ be the probability that an atom in the state 1 will change to the state 2 with absorption of radiation. The coefficients $A_{2 \rightarrow 1}$, $B_{2 \rightarrow 1}$, $B_{1 \rightarrow 2}$ depend only on the atomic states 1 and 2; in particular, they are independent of the temperature.

The relative numbers of atoms in the state 1 and 2, from statistical mechanics, are q_1 and $q_2 e^{-(\chi_1 - \chi_2)/kT}$, where T is the temperature, k is Boltzmann's constant, and q_1, q_2 are the weights of the states 1 and 2. As regards order of magnitude, q_1 and q_2 may be taken to be unity.

In equilibrium, the number of atoms which change from state 1 to state 2 during a time dt must be equal to the number which change from state 2 to state 1. The former number is proportional to

$$q_1 B_{1 \rightarrow 2} I_\nu dt,$$

the latter number to

$$q_2 e^{-(\chi_1 - \chi_2)/kT} (A_{2 \rightarrow 1} + B_{2 \rightarrow 1} I_\nu) dt.$$

Equating these and solving for I_ν , we find

$$I_\nu = \frac{A_{2 \rightarrow 1}}{(q_1/q_2) B_{1 \rightarrow 2} e^{(\chi_1 - \chi_2)/kT} - B_{2 \rightarrow 1}}.$$

This must be the intensity of black radiation of frequency ν at temperature T . When $T \rightarrow \infty$ we must have $I_\nu \rightarrow \infty$, and hence

$$q_1 B_{1 \rightarrow 2} = q_2 B_{2 \rightarrow 1}.$$

This gives

$$I_\nu = \frac{q_2}{q_1} \cdot \frac{A_{2 \rightarrow 1}}{B_{1 \rightarrow 2}} \cdot \frac{1}{e^{(\chi_1 - \chi_2)/kT} - 1}.$$

Applying Wien's law, I_ν must be of the form $\nu^3 f(\nu/T)$. Hence $\chi_1 - \chi_2$ must be proportional to ν , which is Bohr's relation. Further,

$$\frac{q_2}{q_1} \cdot \frac{A_{2 \rightarrow 1}}{B_{1 \rightarrow 2}} \propto \nu^3. \quad \dots \dots (1)$$

We thus arrive at Planck's formula. It is to be noted that had Einstein not assumed the occurrence of out-radiation, he would have arrived merely at the Wien approximation.

Now $A_{2 \rightarrow 1}$ is equal to $1/\tau$, where τ is as before the mean time of excitation of an atom in the state 2 when left to itself, and $B_{1 \rightarrow 2}$ determines the absorption coefficient. Our object is to endeavour to utilize (1) to calculate k_ν .

Einstein, however, in this deduction took no account of the fact that the ν -constituent of black radiation is not homogeneous radiation of intensity ν , but is an element $I_\nu d\nu$ of a continuous spectrum. Thus, if we wish to obtain the numerical form of (1), we must write in our probability definitions $B_{1 \rightarrow 2} I_\nu d\nu dt$, $B_{2 \rightarrow 1} I_\nu d\nu dt$, and we obtain then

$$I_\nu d\nu = \frac{q_2}{q_1} \cdot \frac{A_{2 \rightarrow 1}}{B_{1 \rightarrow 2}} \cdot \frac{1}{e^{h\nu/kT} - 1}.$$

Comparing this with the known value

$$I_\nu d\nu = \frac{2h\nu^3}{c^2} \cdot \frac{d\nu}{e^{h\nu/kT} - 1},$$

we find

$$\frac{B_{1 \rightarrow 2}}{A_{2 \rightarrow 1}} = \frac{q_2}{q_1} \cdot \frac{c^2}{2h\nu^3 d\nu} \dots \dots (2)$$

The magnitude of $d\nu$ is, however, undetermined. It is connected with the amount of the lack of sharpness of fixation of stationary states, which according to Bohr* should be comparable with the radiation during a complete orbital revolution calculated on classical principles. The same method† has, however, been used to calculate the entirely different magnitude τ , by assuming that τ is comparable with the time taken on the classical theory to emit the energy $h\nu$. The proper application of the correspondence principle would appear to be in doubt, though possibly both applications may be right.

* *Zeit. für Phys.* xiii. p. 151 (1923).

† See Foote and Mohler, *loc. cit.* p. 96.

§ 6. Numerical Values.

The connexion between $B_{1\rightarrow 2}$ and the mass absorption coefficient is obtained as follows. Suppose there are N atoms of the kind considered per unit volume, and that on the average the fraction f_1 of these are in the 1-quantum state. Then of the radiation $I_\nu d\nu \cos \theta d\omega dS dt$ incident in time dt , at an angle θ , within a pencil $d\omega$ on a small element of surface area dS and thickness dx , the fraction $k_\nu \rho dx \sec \theta$ will be absorbed, ρ being the density of the atoms considered. In terms of $B_{1\rightarrow 2}$, the amount absorbed is

$$N f_1 dx dS \times B_{1\rightarrow 2} I_\nu d\nu dt \times \frac{d\omega}{4\pi} \times h\nu.$$

Equating the two amounts, we find

$$k_\nu = \frac{B_{1\rightarrow 2} h\nu f_1 N}{4\pi \rho}.$$

But $\rho/N = m'$, the mass of an atom. Hence

$$k_\nu = \frac{B_{1\rightarrow 2} h\nu f_1}{4\pi m'} \quad \dots \quad (2a)$$

Taking the estimate $k_\nu = 10^9$ for the Hg line $\lambda 2537$ ($1S - 2P_2$), for which $f_1 = 1$, $m' = 200 \times 1.64 \times 10^{-24}$, we find

$$B_{1\rightarrow 2} = 0.53. \quad \dots \quad (3)$$

Again, taking the chromospheric estimate $k_\nu = 10^8$ (a lower limit) for the Ca line $\lambda 3933$ ($1\sigma - 1\pi_1$), for which $f_1 = 1$, $m' = 40 \times 1.64 \times 10^{-24}$, we find

$$B_{1\rightarrow 2} = 0.017 \text{ (lower limit)}. \quad \dots \quad (4)$$

For the sake of seeing the order of magnitude given by (2), let us take $\tau = 2 \times 10^{-8}$, whence $A_{2\rightarrow 1} = 0.5 \times 10^8$, and take $d\nu$ to correspond to a range 0.01 A.U. For definiteness take ν to correspond to $\lambda 3000$. Take also $q_1 = q_2 = 1$. We have then $d\nu = 3.3 \times 10^9$; whence from (2)

$$B_{1\rightarrow 2} = 1.0. \quad \dots \quad (5)$$

This is in agreement with (3) as regards order of magnitude, and therefore, in spite of the arbitrariness of our choice of $d\nu$, it must be regarded as confirming the large absolute values of the optical absorption coefficients. Arguments from the correspondence principle indicate smaller values of $d\nu$ than we have assumed, and

thus even larger absorption coefficients. But formula (2) will not be helpful in fixing the exact numerical values until precise definitions and determinations of dv are available.

§ 7. *Continuous Absorption.*

Beyond the limit of any optical series which appears as absorption lines there is in general a region of continuous absorption, which begins fairly abruptly at or near the series limit and fades away towards the violet side*. It has been pointed out by many writers† that towards the head of the series the intensity of the discrete absorption lines passes continuously into the intensity in the region of continuous absorption; actual inspection of spectrograms is very convincing on the point. If therefore we can calculate the absorption coefficient for the latter, we may assume it to give the absorption coefficient for the lines towards the head of the series, and therefore presumably also the order of magnitude of the coefficient for the earlier lines.

In what follows we calculate the absorption coefficient on the assumption that absorption on the high-frequency side of the series limit can only occur through the ejection of photo-electrons; and, similarly, that emission in this region can only occur through the capture of free electrons. Bohr has suggested, however, that transitions may occur, during the encounter of an electron with an atom, from one hyperbolic orbit to another with the emission of radiation; any such transition being a possible one, since hyperbolic orbits are non-quantizable. From the reversibility required by thermodynamic equilibrium it then follows that transitions between hyperbolic orbits must also be possible with the *absorption* of radiation. It would be possible to analyse these transitions in the light of statistical equilibrium. But the formulæ we shall obtain are not vitiated by neglect of processes of this kind; our formulæ in any case give us the absorption coefficient arising from the ejection of photo-electrons. The total absorption coefficient may however, be considerably bigger if absorption by free-free transitions is possible.

* On this subject reference should be made to an interesting letter by Wright, 'Nature,' June 24th, 1920, p. 810.

† E.g., Sommerfeld, 'Atomic Structure and Spectral Lines,' p. 448 (1923).

§ 8. Statistical Analysis of the Photo-electric Liberation of Electrons.

Let us consider a quantity of partially ionized gas in dissociative equilibrium in an enclosure at a given temperature. Let the ionization potential be χ . For simplicity we will assume in the first instance that the gas consists of atoms of a single kind, that each neutral atom is capable of only one stationary state (so that each atom either is ionized or has its outermost electron in the state corresponding to negative energy χ), and that the amount of second or higher-stage ionization is inappreciable. These restrictions will be removed later. The atoms will be slow-moving compared with the free electrons. To a sufficient degree of approximation we can ignore the velocity of an atom in comparison with that of an electron encountering it.

Let N be the number of atoms per unit volume, x the degree of ionization, P the pressure, T the temperature, k the gas-constant per molecule (Boltzmann's constant), h Planck's constant, m the mass of an electron. Let g be the "weight" of the stationary state. Then the degree of ionization is given by the thermodynamic or statistical formula *

$$\frac{x^2}{1-x} P = T^{5/2} e^{-\chi/kT} \frac{(2\pi m)^{3/2} k^{5/2} \sigma}{g h^3} \quad (6)$$

Here σ is the symmetry number of the neutral atom; it is equal to the number of equivalent electrons capable of being removed in first-stage ionization.

Let $\psi(\nu) I_\nu d\nu dt$ be the probability that a neutral atom will in time dt , under the influence of isotropic ν -radiation of intensity $I_\nu d\nu$, become ionized by absorption of a quantum of energy $h\nu$. The velocity v of the ejected electron is given by Einstein's law of the photo-electric effect,

$$h\nu = \frac{1}{2}mv^2 + \chi \quad (7)$$

Since $N(1-x)$ is the number of neutral atoms, the total number of ν -quanta absorbed in time dt is

$$N(1-x) \psi(\nu) I_\nu d\nu dt \quad (8)$$

Consider now the encounter with an ionized atom. We wish to calculate the number of encounters, with ionized

* For its most general derivation, see R. H. Fowler, *Phil. Mag.* xlv. p. 21 (1923). In virtue of our assumption of only one stationary state, the partition function $b(T)$ reduces to g . For the introduction of the symmetry number σ , see Fowler and Milne, 'Monthly Notices R. A. S.' lxxxiii. p. 107 (1923).

atoms, of electrons having velocities between v and $v + dv$, where the velocity-range dv is connected with the frequency range $d\nu$ by the relation

$$h d\nu = mv dv \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

obtained by differentiation of (7).

The number of free electrons per unit volume is Nx . By a known formula from gas-theory, according to Maxwell's law, the number of electrons with velocities between v and $v + dv$ and with velocity-directions lying inside an elementary solid angle $d\omega$ is

$$Nx \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^2 dv d\omega.$$

We fix attention on v -electrons whose paths before encounter are so situated as to pass a given atom at a distance lying between p and $p + dp$. The number of such electrons encountering the given atom in time dt whose velocity-directions lie within a given cone $d\omega$ is

$$Nx \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^2 dv d\omega \times 2\pi p dp \times v dt,$$

and hence the total number in all directions is

$$8\pi^2 Nx \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^3 dv p dp dt.$$

The number of ionized atoms per unit volume is Nx , and hence the total number of $(v, v + dv; p, p + dp)$ encounters is

$$8\pi^2 N^2 x^2 \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^3 dv p dp dt.$$

Now let $f(v, p)$ be the probability that a (v, p) encounter results in capture. Then the number of captures in time dt is

$$8\pi^2 N^2 x^2 \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} F(v) v^3 dv dt, \quad . \quad (10)$$

where

$$F(v) = \int_0^{p_0} f(v, p) p dp,$$

p_0 being the effective radius of the atom for capture-encounters; i. e., p_0 is defined by the relation

$$f(v, p) = 0, \quad (p > p_0).$$

In general, p_0 will be a function of v . If we write

$$\int_0^{p_0} f(v, p) 2\pi p dp = \pi s^2,$$

$$F(v) = \frac{1}{2}s^2,$$

then s is in Eddington's terminology * the "effective target radius"; for if the atom offered an actual target of radius s , we should have

$$f(v, p) = 1, \quad (0 < p < s);$$

$$f(v, p) = 0, \quad (p > s).$$

In equilibrium the number of ionizations with emission of v -electrons must be equal to the number of recombinations with r -electrons †. Equating (8) and (10), we have

$$N(1-x)\psi(v)I_\nu dv dt$$

$$= 8\pi^2 N^2 x^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2}mv^2/kT} F(v) v^3 dv dt. \quad (11)$$

Now the total pressure P is given by

$$P = N(1+x)kT.$$

Inserting this in (11) and using the relation (9) between dv and $d\nu$, we find that (11) gives an equation for x which will be identical with the dissociation formula (6), provided

$$I_\nu = \frac{8\pi^2 m^2 \sigma v^2 F(v)}{qh^2 \psi(v)} e^{-(\frac{1}{2}mv^2 + \chi)/kT}$$

$$= \frac{8\pi^2 m^2 \sigma v^2 F(v)}{qh^2 \psi(v)} e^{-h\nu/kT}. \quad (12)$$

But I_ν must be the intensity of black radiation,

$$I_\nu = \frac{2h\nu^3}{c^2} \cdot \frac{1}{e^{h\nu/kT} - 1}. \quad (13)$$

Identifying these, we have

$$\psi(v) = \frac{4\pi^2 m^2 \sigma v^2 F(v)}{qc} \left(\frac{c}{h\nu}\right)^3 (1 - e^{-h\nu/kT}), \quad (14)$$

where it should be remembered that v is connected with ν by relation (7).

* 'Monthly Notices,' lxxxiii. p. 35 (1922); lxxxiii. p. 431 (1923).

† The argument here is entirely independent of the extent to which ionization occurs by collision. See § 15 below.

§ 9. *Necessity for assuming that Capture can be stimulated by Radiation.*

Our object being to determine $\psi(\nu)$, equation (14) should contain the answer to the problem. But it makes $\psi(\nu)$ depend on the temperature, whereas $\psi(\nu)$ was defined as an atomic property, strictly independent of statistical variables such as the temperature. Our hypotheses have therefore led to a contradiction. It was to avoid a contradiction of this kind that Einstein made his assumption of "out-radiation," and we can obtain a form for $\psi(\nu)$ strictly independent of temperature by introducing an analogous assumption. We are compelled to suppose that external radiation can stimulate the capture of an electron, and we therefore assume that *there is an additional probability $g(r, p) I_\nu$ that a (r, p) encounter will result in capture with emission of ν -radiation, v and ν being connected by relation (7)* Write then

$$\int_0^{p_0} g(r, p) p dp = G(v).$$

Carrying through the analysis as before, we find that equation (12) becomes replaced by

$$I_\nu = \frac{8\pi^2 m^2 \sigma v^2 [F(r) + I_\nu G(r)] e^{-h\nu/kT}}{q h^2 \psi(\nu)} \dots (12')$$

Solving for I_ν , we find

$$I_\nu = \frac{8\pi^2 m^2 \sigma v^2 F(v)}{q h^2 \psi(\nu) e^{h\nu/kT} - 8\pi^2 m^2 \sigma v^2 G(r)} \dots (15)$$

This will be identical with (13), provided

$$\frac{F(r)}{G(r)} = \frac{2h\nu^3}{c^2} \dots (16)$$

and

$$\psi(\nu) = \frac{4\pi^2 m^2 \sigma v^2 F(r)}{q c} \left(\frac{c}{h\nu} \right)^3 \dots (17)$$

Formula (17) gives $\psi(\nu)$ independent of T , thus removing the contradiction.

The ratio of the number of stimulated captures to the number of unstimulated captures is

$$\frac{G(r) I_\nu}{F(r)} = \frac{1}{e^{h\nu/kT} - 1}.$$

For the region of the spectrum in the neighbourhood of $\lambda_{\max}$, $h\nu/kT$ is about 5; so that in this region, and *a fortiori* for all higher frequencies, the proportion of stimulated captures is negligible. For low frequencies the ratio approximates to $kT/h\nu$, and so the stimulated captures are the important ones. But, of course, frequencies lower than χ/h do not come into consideration.

It will be seen that if either the radiation formula (13) or the dissociation formula (6) is known, the present method affords a means of deducing one of these from the other.

§ 10. Extension to Atoms capable of a Number of Stationary States.

Let the numerals 1, 2, ... denote the possible stationary states of a given neutral atom, arranged in order of decreasing negative energy. Let $\chi^{(1)}, \chi^{(2)}$ denote the (negative) energies of the levels; $\chi^{(1)}$ is now the ionization potential. Let $q_1, q_2, \dots$ be the "weights" of the corresponding states. Then the fraction f_r of neutral atoms which are in the state r is given by

$$f_r = \frac{q_r e^{-(\chi^{(1)} - \chi^{(r)})/kT}}{b(T)}, \dots \dots \dots (18)$$

where $b(T)$ is the partition function defined by

$$b(T) = q_1 + q_2 e^{-(\chi^{(1)} - \chi^{(2)})/kT} + q_3 e^{-(\chi^{(1)} - \chi^{(3)})/kT} + \dots$$

Also the degree of ionization is given by

$$\frac{x^2}{1-x^2} P = T^{5/2} e^{-\chi^{(1)}/kT} \frac{(2\pi m)^{3/2} k^{5/2} \sigma}{h^3 b(T)}. \dots \dots (19)$$

When an ionized atom captures an electron, the electron may be bound in any one of the stationary states. To every such state there corresponds a series limit, which we will denote by $\nu^{(r)}$, given by $h\nu^{(r)} = \chi^{(r)}$. The binding of an electron in the r -state will result in the emission of radiation of frequency $\nu > \nu^{(r)}$. Similarly for absorption, the gas will be capable of giving a series of continuous absorption bands, one for each $\nu^{(r)}$.

We use $\psi^{(r)}(\nu)$, $F^{(r)}(\nu)$, $G^{(r)}(\nu)$ in our probability definitions. Equating the number of photo-electric ejections

from the r -state to the number of bindings into the r -state *, we find

$$\begin{aligned} & f_r N (1-x) \psi^{(r)}(\nu) I_\nu d\nu dt \\ &= 8\pi^2 N^2 x^2 \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} [F^{(r)}(v) + I_\nu G^{(r)}(v)] v^3 dv dt. \end{aligned}$$

On using (18) and (19), the function $b(T)$ cancels out, and we find

$$\psi^{(r)}(\nu) = \frac{4\pi^2 m^2 \sigma v^2 F^{(r)}(r)}{q_r c} \cdot \left(\frac{c}{h\nu} \right)^3, \quad \dots \quad (20)$$

where v and ν are now connected by the relation

$$h\nu = \frac{1}{2}mv^2 + \chi^{(r)}.$$

The only effect of the generalization to a number of stationary states is seen by comparison of (17) and (20) to be the introduction of the appropriate weight q_r .

§ 11. *Extension to Multiple Ionization and to Mixtures.*

Let $\chi_1, \chi_2, \dots$ be the successive ionization potentials, *i. e.* the potentials corresponding to the removal, in the order mentioned, of the 1st, 2nd, ... electrons. (χ_1 is identical with the $\chi^{(1)}$ of § 10.) Let P_e be the partial pressure of electrons. Let x_r be the fraction of atoms whose ionization potential is χ_r , *i. e.* which have already lost $(r-1)$ electrons. The dissociation formula is

$$\frac{x_{r+1}}{x_r} P_e = T^{5/2} e^{-\chi_r/kT} \frac{(2\pi m)^{3/2} k^{5/2} \sigma_r}{q_r h^3}, \quad \dots \quad (21)$$

σ_r being the symmetry number and q_r the weight of the $(r-1)$ -fold ionized atom. For equilibrium we must have

$$\begin{aligned} & x_r N \psi_r(\nu) I_\nu d\nu dt \\ &= 8\pi^2 x_{r+1} N N_e \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} [F_r(r) + I_\nu G_r(r)] v^3 dv dt, \end{aligned}$$

where N_e , the number of free electrons per unit volume, is given by

$$P_e = N_e kT.$$

* The number of ejections from the r -state to another stationary state are balanced by the number of gains by the r -state from other stationary states, Einstein's investigation holding for these. If the two kinds of gains and losses did not balance separately, the pressure would be involved differently for the two kinds, and we should get a discrepancy on combining with the radiation and dissociation formulae.

On eliminating x_{r+1}/x_r , we arrive at the relation *

$$\psi_r(v) = \frac{4\pi^2 m^2 \sigma_r v^2 F_r(v)}{qrc} \cdot \left(\frac{c}{hv}\right)^3, \quad \dots \quad (22)$$

where

$$hv = \frac{1}{2}mv^2 + \chi_r.$$

In this formula $\psi_r(v)$ refers to the probability of absorption by the $(r-1)$ -fold ionized atom with loss of an electron, $F_r(v)$, to the probability of capture by the r -fold ionized atom.

It will be noticed that in deducing (22) we have not assumed that the free electrons were derived only from ionization of the atoms in question; there has been no need to know the value of P_r . It follows that (22) holds also for a mixture of different kinds of atoms, ionized to any extent. Indeed this must be so, since (22) expresses a property of the atom itself, ψ and F being atomic functions.

§ 12. The Probability of Electron Capture.

At the series limit the velocity of ejection of the photo-electron is zero. Hence we have

$$\psi_r(v_r) = \frac{4\pi^2 m^2 \sigma_r}{qrc} \cdot \left(\frac{c}{hv_r}\right)^3 \lim_{v \rightarrow 0} v^2 F_r(v). \quad \dots \quad (23)$$

Inspection of spectrograms shows that at and near the limit the absorption has a perfectly definite value, not zero and of course not infinite. Hence, from (23), $v^2 F(v)$ must have a finite non-zero limit as $v \rightarrow 0$. This means that *for small speeds the probability of capture must obey approximately a law of the type*

$$F(v) = \frac{\text{const.}}{v^2}. \quad \dots \quad (24)$$

It has been suggested by Eddington† that an electron is captured when it actually "hits the nucleus"; and using the inverse square law of force and taking account of relativity mechanics, he has given the formula

$$\begin{aligned} F(v) &= \frac{1}{2}s^2 = \frac{Zb(d + \frac{1}{2}Zb)r^2}{v^2} \\ &= \mu/v^2, \quad \dots \quad (25) \end{aligned}$$

* We have for simplicity omitted the generalization arising from the possibility of the $(r-1)$ -fold ionized atom possessing a number of stationary states. It would be easy to take account of the corresponding weights if required.

† *Loc. cit.*

say, where Z is the atomic number, d is the radius of the nucleus, and b is a constant given by

$$b = e^2/mc^2 = 2.81 \times 10^{-13} \text{ cm.}$$

It will be seen that this is of the form (24).

The validity of the assumption that capture depends on colliding with the nucleus has been criticized, but Eddington has shown that formula (25) leads to a value for the mean coefficient of absorption for stellar material in the interior of a star which is in agreement with the value he has deduced from the observed masses and luminosities of the stars. We shall return to the stellar absorption coefficient in § 15, but in the meantime we shall tentatively adopt Eddington's formula (25) as a working specification for $F(v)$. In doing so we are not necessarily adopting a nuclear-collision hypothesis: we are simply assuming that the probability of capture is inversely proportional to the square of the velocity not merely for small speeds (which we have shown independently to be the case), but for all the speeds we desire to consider; and that further the constant of proportionality has the numerical value deduced by Eddington.

§ 13. *Numerical Applications. Test of the Inverse Square Law.*

We will first apply formula (20) with $F(v)$ given by (25) to the continuous spectrum lying beyond the Balmer limit in the hydrogen spectrum. The atoms absorbing the Balmer lines or the associated continuous spectrum are in the second quantum state, and for hydrogen we have $q_r = r(r+1)$, so that $q_2 = 6$. For simplicity take $\lambda = 3000 \text{ A.U.}$ (the limit of the Balmer series is $\lambda 3647$). In (25) we take $Z=1$, and there is no need to evaluate v , since with the inverse square law the function $v^2 F(v)$ occurring in the formula for $\psi(v)$ is independent of v . We have $\sigma=1$, $h=6.55 \times 10^{-27}$, $c=3 \times 10^{10}$, $m=9.00 \cdot 10^{-28}$. For the "radius of the nucleus" we may conveniently adopt the "radius of the electron"

$$d = \frac{2}{3} e^2/mc^2 = 1.87 \times 10^{-13} \text{ cm.}$$

We find then

$$F(v) = \frac{0.83 \times 10^{-4}}{v^2},$$

whence

$$\psi^{(2)}(v) = 1.4 \times 10^{-3} \dots \dots \dots (26)$$

The corresponding value of the mass absorption coefficient k ,

for a hypothetical mass of hydrogen all in the 2-quantum state is given by

$$k_{\nu} = \frac{\psi^{(2)}(\nu) h\nu}{4\pi m'} = 4.5 \times 10^8$$

(using $m' = 1.64 \times 10^{-24}$). This is of the order of magnitude of the observed monochromatic coefficient for mercury and the chromospheric coefficient for ionized calcium*.

For $Z=80$, (Hg), taking now $q=1$ for the weight, we find similarly for $\lambda 3000$

$$\psi(\nu) = 23.4,$$

and for $Z=20$, (Ca), we find

$$\psi(\nu) = 1.55.$$

These are considerably larger than the corresponding *monochromatic* probabilities calculated in § 6, results (3) and (4). Eddington's formula (25) makes μ practically proportional to Z^2 , and so gives an enormously increased chance of capture for elements of high atomic number. But it must be remembered that we are considering for the moment the capture of an electron into the optical levels of a neutral (or almost neutral) atom, and the screening due to the other electrons may in this case reduce the effective atomic number for capture purposes. The stellar absorption coefficient is perhaps better given by the formula deduced by Eddington for non-relativistic orbits, which makes μ proportional to Z simply. If we increase the value of $\psi(\nu)$ for hydrogen simply in the ratio of the atomic numbers and

* It may be mentioned here that in some unpublished investigations the author has deduced from the observed temperature of the stars in which the Balmer lines reach their maximum ($10,000^\circ$) that in these stars

$$\frac{B_{2 \rightarrow n} h\nu}{4\pi m'} \cdot \frac{\omega}{g} = 3.6 \times 10^2,$$

where g is the effective value of gravity at the surface of the star and ω is the proportion by mass of hydrogen in the layer in which the Balmer lines originate. For such stars we may take $g=2 \times 10^3$. We are entirely uncertain as to the proportion of hydrogen, but if for definiteness we take $\omega=10^{-2}$ (one per cent. by mass—a reasonable value) we find for the Balmer lines

$$k_{\nu} = \frac{B_{2 \rightarrow n} h\nu}{4\pi m'} = 0.7 \times 10^8.$$

This "astronomical value" of the monochromatic absorption coefficient is of the order of magnitude calculated in the text for the continuous spectrum.

multiply by 6 for the change of q , we find for Hg

$$\psi(\nu) = 0.68,$$

and for Ca

$$\psi(\nu) = 0.17.$$

These numbers are in general agreement with the estimates of the monochromatic probabilities.

Whatever the precise mode of dependence on atomic number—the data are quite insufficient to decide this point,—it is clear that the photo-electric absorption coefficients are very high, and that the calculation confirms the general order of magnitude of the monochromatic absorption coefficients. We have seen that $F(\nu)$ must be proportional to ν^{-2} for small values of ν ; we are now entitled to say that an inverse square capture-formula of Eddington's type simultaneously allows us to deduce optical coefficients, of the order of 10^9 , and the stellar absorption coefficient, of the order of 40. The apparent range of validity of this formula for $F(\nu)$ is the more striking when we reflect that in the interior of a star the electronic velocities are of the order of 1.6×10^9 cm.sec.⁻¹, (720 volts), corresponding to a temperature of 5.6×10^6 degrees, whilst for the hydrogen atom, with $\chi^{(2)} = 3.39$ volts, the velocity of the photo-electron for $\lambda 3000$ is 5.1×10^7 cm.sec.⁻¹; for the Balmer limit itself the velocity is, of course, zero. It is to be expected that for high speeds, $F(\nu)$ will vary more rapidly with ν than the inverse square; but a departure from the inverse square in this direction in the velocity range here considered would lead to still higher values for the deduced optical coefficients, or conversely, assuming the optical coefficients, to a much smaller value for the stellar coefficient than is observed.

Whether this discussion affords genuine evidence for the validity of the inverse square law for the probability of capture over a considerable range of velocities can hardly be said definitely, but the writer is inclined to believe that it does. The results at least justify our continuing tentatively to adopt the inverse square law.

§ 14. *Inferences from the Inverse Square Law.*

If the inverse square law holds, we have immediately

$$\psi(\nu) \propto \nu^{-2}, \quad k_\nu \propto \nu^{-2},$$

for the law of absorption in the region beyond the series limit. This could presumably be tested by actual experiment.

Such experiments would afford valuable evidence as to the validity of the inverse square law if they could be carried to sufficiently high frequencies.

It may be recalled that the law of absorption of X-rays by matter on the high-frequency side of a limit is $k \propto \lambda^2 \propto \nu^{-2}$, which differs from our law for the optical case. The two are however in no way analogous; it is apparent, in fact, that considerations of statistical equilibrium on the foregoing lines can of themselves give no information concerning X-ray absorption until the temperature is so high that the ordinary temperature radiation contains X-ray frequencies in appreciable amounts, in which case however (as in the interior of a star) there would be intense ionization, the outer electrons would be largely stripped off, and the X-ray levels would play the part of optical levels *. (See § 18.)

The thermodynamics of the interaction of X-rays and matter has been considered by L. de Broglie†, and employed in an attempt to deduce the law $k \propto \lambda^3$ for the absorption of X-rays. In one part of his paper he envisages strict thermodynamic equilibrium, and obtains a formula for the probability of capture in terms of the absorption coefficient; he uses however not the dissociation formula, but Richardson's thermionic formula for the density of free electrons in an enclosure. But in the later parts of his paper he balances a fraction of the energy absorbed in the continuous absorption band against the energy emitted in the line spectrum, thereby violating the details of strict thermodynamic equilibrium. Further, to obtain the absorption law $k \propto \lambda^3$ he finds it necessary to introduce certain additional arbitrary assumptions. It is true that the absorption of an X-ray frequency by a normal atom with ejection of an electron from an inner level is followed, and probably followed very rapidly, by a series of monochromatic emissions as the electrons in the outer levels fall in; but in thermodynamic equilibrium each event must be reversible. If the successive events are linked in an unalterable sequence, as is likely in this case, then we are bound to regard them as forming a single event capable of occurring in the reverse direction—a succession of discrete absorptions followed by an emission; and it is the numbers of forward and backward events that must be balanced. This assumes, as seems probable, that the principle of the separate balancing of reversible events in thermodynamic equilibrium, which we have already seen to be necessary in certain cases,

* The λ^3 law would require a capture-probability function varying as the inverse fourth power of the velocity for high velocities.

† *Journ. de Physique*, iii. p. 33 (1922).

can be given a wider generalization, and invoked in cases where direct arguments from pressures and temperatures as to the independent balancing are not available.

For the monochromatic absorption-probability we found in § 5, equation (2),

$$B_{i \rightarrow n} = \frac{c^2}{2h\nu^3 d\nu} \cdot \frac{q_n}{q_1} A_{n \rightarrow 1}.$$

The value of $B_{i \rightarrow n}$ near the head of the series should pass continuously into the value of $\psi(\nu)$ given by (20). It will be noted that ν^3 occurs in the denominator of both expressions. Hence for large quantum numbers we should expect

$$\frac{q_n A_{n \rightarrow 1}}{d\nu} = \text{constant},$$

since here we may certainly take $\nu^2 F(\nu)$ as constant.

Concerning $d\nu$, since $h\nu = \chi^{(1)} - \chi^{(n)}$ the breadth of the line will depend on the limits of fixation of both the stationary states 1 and n . But for large n the energy values of the successive stationary states are close together, and the classical radiation from them would be small; hence we may suppose that $d\nu$ arises almost entirely from the limits of the state 1. In that case $d\nu$ will be independent of n when n is large, and hence for large n we should have

$$q_n A_{n \rightarrow 1} = \text{constant}.$$

Since for hydrogen $q_n = n(n+1)$, this would give for large n

$$\tau = \frac{1}{A_{n \rightarrow 1}} \propto n^2.$$

The rate of radiation from an orbit on the classical theory is proportional to n^{-8} , so that the assumption that it is the latter principle which determines τ is inconsistent with the result we have obtained from consideration of the continuity of transition from the binding of external electrons to the falling-in of electrons from orbits of large quantum number. The case for this continuity seems unassailable, and therefore either τ is not determined from the classical radiation, or else the assumption we have introduced about $d\nu$ is untenable. We shall not pursue this matter further.

§ 15. The Rate of Ionization.

By definition of $\psi(\nu)$, the total number of photo-electric ionizations per atom per second, in equilibrium, is

$$\int_{\nu_1}^{\infty} \psi(\nu) I_{\nu} d\nu,$$

where ν_1 is the series limit for the initial state concerned. Inserting for $\psi(\nu)$ and assuming the inverse square law, this becomes

$$\frac{8\pi^2 m^2 \sigma \mu}{q h^2} \int_{\nu_1}^{\infty} \frac{d\nu}{e^{h\nu/kT} - 1},$$

and provided χ/kT is not too small, this may be written approximately

$$\frac{8\pi^2 m^2 \sigma \mu}{q h^3} kT e^{-\chi/kT}.$$

For hydrogen at 10,000°, the number of photo-electric ionizations per second of an atom in the 2-quantum state is found to be

$$0.84 \times 10^8,$$

where we have taken $\chi = 3.39$ volts, and $q = 6$. Of course, at this temperature comparatively few of the neutral atoms are in other than the normal state; the fraction in the 2-quantum state is in fact 2.2×10^{-5} . The foregoing result is therefore best stated in the form that once an atom has been excited into the 2-quantum state, its average life in that state, as limited by photo-electric ionization, is about 10^{-8} sec. Other agencies of destruction, besides its own intrinsic tendency to return to the normal state, will naturally shorten this.

§ 16.

The Mean Absorption Coefficient for Highly-ionized Material at High Temperatures, averaged through the Spectrum.

For the coming-away of the r th electron we have obtained the formula

$$\psi_r(\nu) = \frac{4\pi^2 m^2 \sigma_r r^2 F_r(r)}{q r c} \left(\frac{c}{h\nu} \right)^3.$$

The fraction of atoms $(r-1)$ -fold ionized and therefore in a position to lose the r th electron is x_r . Hence the contribution to the total mass-absorption coefficient due to these atoms is

$$k_r(\nu) = \frac{h\nu}{4\pi m} x_r \psi_r(\nu). \quad \dots \quad (27)$$

This holds for $\nu > \nu_r$, where $h\nu_r = \chi_r$. For $\nu < \nu_r$ the r -atoms are transparent, save for line-absorption due to the different stationary states of the $(r-1)$ -fold ionized atom. We shall omit any such line-absorption from consideration. This is equivalent to regarding each atom as possessing only one stationary state for each degree of ionization, though presumably each ionized "kernel" possesses a series of "optical" levels. However, we are determining only the continuous absorption, and are regarding the absorption coefficient of the material as a whole as due to the superposition of regions of continuous absorption arising from the loss of photo-electrons.

Suppose, now, that the probability of capture is the same for all stages of ionization*, i. e. suppose $F_r(r)$ the same for all r . Then the absorption coefficient of the whole material for frequency ν is given by

$$k(\nu) = \sum k_r(\nu) = \frac{\pi m^2 r^2 F(r)}{m'} \left(\frac{c}{h\nu} \right)^2 \sum_{r=1}^{\infty} \frac{\sigma_r x_r}{q_r}, \quad (28)$$

the summation being extended to all r 's for which $\chi_r < h\nu$. Thus for large ν , atoms in almost all stages of ionization will contribute, but for small ν , only atoms in the earlier ones can do so. Atoms in the earlier stages of ionization are effective throughout the greater part of the spectrum, atoms in the later stages only through the region of high frequencies. For high frequencies, therefore, the absorption coefficient of the whole mass varies as ν^{-2} , but as the frequency decreases, the absorption coefficient changes less rapidly, owing to the dropping-out of the more highly-ionized atoms. It would be an easy matter to obtain the march of $k(\nu)$ in any particular case, given the ionization potentials and the pressure and temperature.

To find the mean absorption coefficient, we must integrate through the spectrum. The mean absorption coefficient for black radiation is

$$\bar{k} = \int_0^{\infty} k(\nu) I_\nu d\nu / \int_0^{\infty} I_\nu d\nu,$$

but in our case the contribution from atoms in any given stage of ionization must be integrated only through the

* With Eddington's nuclear-collision theory of capture, this assumption holds; for $F(r)$ then depends only on the atomic number.

range of spectrum in which they are effective. We have then

$$k_r = \frac{\pi m^2 c^2 \sigma_r x_r}{m' q_r} \frac{\int_{\nu_r}^{\infty} \nu^2 F(\nu) (h\nu)^{-2} I_\nu d\nu}{\int_0^{\infty} I_\nu d\nu}.$$

Assuming the inverse square law, we put $\nu^2 F(\nu) = \mu$ and take it outside the sign of integration. Introducing Planck's formula for I_ν , we have

$$\bar{k}_r = \frac{\pi m^2 c^2 \mu \sigma_r x_r}{m' k^2 \Gamma^2 q_r} \int_{y_r}^{\infty} \frac{y dy}{e^y - 1} \bigg/ \int_0^{\infty} \frac{y^3 dy}{e^y - 1},$$

where

$$y = \frac{h\nu}{kT}, \quad y_r = \frac{h\nu_r}{kT} = \frac{\chi_r}{kT}.$$

The integral in the denominator has the value $\pi^4/15$. For that in the numerator put

$$\int_{y_r}^{\infty} \frac{y dy}{e^y - 1} = e^{-y_r} \xi(y_r).$$

It is readily found that for y small

$$\xi(y) \sim \frac{1}{6}\pi^2 + y(\frac{1}{6}\pi^2 - 1),$$

and that for y large

$$\xi(y) \sim 1 + y.$$

The error of the latter approximation is only 5 per cent. for y so small as 2.

We have now

$$\bar{k}_r = \frac{15m^2 c^2 \mu}{\pi^3 m' k^2 \Gamma^2} \frac{\sigma_r x_r}{q_r} e^{-y_r} \xi(y_r).$$

We can eliminate $\sigma_r x_r e^{-y_r}/q_r$ from this by means of the dissociation formula (21). We find then

$$\bar{k}_r = \frac{P_e}{(kT)^{9/2}} \cdot \frac{15c^2 \mu h^3}{2\pi^4 m'} \left(\frac{m}{2\pi}\right)^{1/2} x_{r+1} \xi(y_r), \quad \dots \quad (29)$$

a formula which shows how the part of the absorption coefficient due to the $(r-1)$ -fold ionized atoms depends on the number of r -fold ionized atoms available for the compensating process of capture.

Summing for the whole material, we have

$$k = \frac{P_e}{(kT)^{3/2}} \cdot \frac{15c^2\mu h^3}{2\pi^4 m'} \left(\frac{m}{2\pi}\right)^{1/2} \sum_{r=1}^{\infty} x_{r+1} \xi(\chi_r/kT). \quad (30)$$

This is the complete expression for the mean absorption coefficient in terms of the pressure and temperature and the successive ionization potentials.

§ 17. Comparison with Eddington's Formula for k .

A theoretical calculation of k was first given by Eddington*. His method, involving the consideration of "electron lives," is the same in principle as that used in this paper, though it does not have regard to the finer details of the statistical equilibrium. He throughout worked with mean values—the mean velocity of an electron at temperature T , the mean value of a quantum at temperature T —and thus took no account of the dependence on frequency. Again, he treated all the atoms as on the same footing as regards their encounters with electrons. The present method takes account of the various amounts of ionization and of the various regions of the spectrum to which the atoms of various degrees of ionization contribute, and it is through this that our factor involving ionization potentials arises. It will be interesting to compare the formulæ in detail.

If A is the atomic weight of the element considered, M the mean molecular weight of the ionized system, m_H the mass of a hydrogen atom (so that $m' = Am_H$), the ratio of the number of free electrons to the number of atoms is $(A/M) - 1$, and hence, if ρ is the density,

$$P_e = \left(\frac{A}{M} - 1\right) \frac{\rho kT}{Am_H}.$$

Hence

$$k = \frac{15\mu c^2 h^3}{2\pi^4 A m_H^2} \left(\frac{m}{2\pi}\right)^{1/2} \left(\frac{1}{M} - \frac{1}{A}\right) \frac{\rho}{(kT)^{3/2}} \sum_{r=1}^{\infty} x_{r+1} \xi(\chi_r/kT). \quad (31)$$

Eddington's value in our notation is

$$\bar{k}_{\text{Edd.}} = \frac{2\pi\mu k}{A m_H^2 a c M} \cdot \frac{\rho}{T^{3/2}} \times 2.70.$$

Here a is such that aT^4 is the energy density of black radiation, and so

$$a = \frac{8\pi^5}{15} \cdot \frac{k^4}{h^3 c^3};$$

* 'Monthly Notices,' lxxxiii. p. 32 (1922).

and u is the harmonic mean velocity of an electron at 1° absolute, and so

$$u = (\pi k/2m)^{1/2}.$$

We have then

$$k_{\text{Edd.}} = \frac{15\mu c^2 h^3}{2\pi^4 m_H^2 A} \left(\frac{m}{2\pi}\right)^{1/2} \frac{1}{M} \cdot \frac{\rho}{(kT)^{3/2}} \times 2.70. \quad (32)$$

Eddington uses the value $\mu = Zbc^2(d + \frac{1}{2}Zb)$, derived on the nuclear-collision hypothesis, but for the purpose of comparison we have preferred to leave μ unformulated, assuming only the inverse square law for the probability of capture.

It is seen on comparison of (31) and (32) that our more detailed method confirms Eddington's formula completely*, save for his factor 2.70 replacing our summation factor. This arises in Eddington's treatment from the use of the mean quantum at temperature T , which is equal to $2.70 kT$, the numerical factor being found from the relation

$$\frac{h\nu}{kT} = \int_0^\infty \frac{y^3 dy}{e^y - 1} / \int_0^\infty \frac{y^2 dy}{e^y - 1} = 2.70.$$

The numerical value of our summation factor is considered in § 18.

It has been argued by Lindemann† that Eddington's method is vitiated by the fact that he took no account of the electrons liberated by collision, tracing all the free electrons present to the action of radiation; that vastly greater numbers would be liberated per second by collisions; and that hence the mean free path of an electron would be smaller and thus the calculated "effective target area" (the quantity πs^2 of § 8) much larger to give the same observed absorption coefficient. Eddington, whilst denying that the amount of energy available for setting electrons free permits a number of captures appreciably different from the number he has calculated, yet remarks‡ that he would be "glad of data which would enable an estimate to be made of the number of additional electrons set free by collisions, so as to take account of the necessary correction if appreciable."

The method and results of the present paper show that the validity of Eddington's procedure (when refined so as

* The ionization being large, Eddington specifically neglects $1/A$ in comparison with $1/M$.

† 'Observatory,' xlv. p. 384 (1922); 'Monthly Notices,' lxxxiii. p. 332 (1923).

‡ 'Monthly Notices,' lxxxiii. p. 436 (1923).

to take account of the absorption coefficient as a function of frequency) is entirely independent of the extent to which ionization by collision occurs. The number of electrons free at any one instant is determined purely by considerations of probability and thermodynamics; dissociation must proceed to such an extent that the entropy is a maximum, whatever the mechanism of dissociation. Electrons may be (and almost certainly are) liberated in enormous numbers by collisions*; but such collisions have no effect whatever on the number free at any one instant, when the gas is in thermodynamic equilibrium. In so far as free electrons are produced by photo-electric action with absorption of radiation, they will be recaptured, to exactly the same extent, with the emission of radiation; in so far as free electrons are produced by collision between two bodies (say between an atom and an electron), to exactly the same extent they will be recombined by radiationless three-body encounters (of the ion, the electron to be bound, and another electron). A form of equilibrium might be imagined to exist in which the two sets of processes did not separately balance; but it would not lead to the thermodynamic dissociation formula. The equilibrium would, in fact, involve the pressure through a factor of the form

$$\frac{a_2 P^2 + b_2 P^3}{a_1 P + b_1 P^2},$$

in which the ratio of a_2/a_1 to b_2/b_1 would depend on the relative efficiency of the two processes. This is incompatible with the deduction of thermodynamics; we must have therefore $a_2/a_1 = b_2/b_1$, and the processes balance separately. We have seen, indeed, that for strict thermodynamic equilibrium it is necessary to suppose that captures are to some extent stimulated by external radiation, more particularly that a capture with emission of radiation of frequency ν is rendered more probable by the presence of external radiation of frequency ν ; but this does not affect the independence of the mechanisms or the form of the final expression for the absorption coefficient.

§ 18. *The Ionization-Potential Correcting Factor.*

It is easy to see in a general way the order of magnitude of the factor

$$\Sigma = \sum_{r=1} x_{r+1} \xi(\chi_r/kT)$$

* See Mr. R. H. Fowler's paper in the next number of this Magazine, § 5.

and of the significant ionization-potentials. Were the temperature so high that all the atoms were practically ionized down to their nuclei, χ_r/kT would be small for all values of r , and the value of Σ would be $\pi^2/6$ in each case. We should then have, since $\sum_1 x_r = 1$,

$$\Sigma = \frac{1}{6}\pi^2 \sum_{r=1} x_{r+1} = \frac{1}{6}\pi^2(1-x_1) = \frac{1}{6}\pi^2,$$

for x_1 , the fraction remaining neutral, must be negligible. The value of $\pi^2/6$ is 1.645, which is therefore the factor replacing Eddington's factor 2.70 in this case. For example, we could find in this way the opacity of hydrogen at a temperature so high that it was practically a mass of protons. It might be expected that under such circumstances the gas would be practically transparent, but the value comes out of the same order of magnitude as the stellar absorption coefficient for the same density and temperature. Comparatively few of the nuclei at any one instant possess an electron with which to absorb, but each one that does so possesses in effect the large-valued optical absorption coefficient.

When the temperature is not so high as this, a fair approximation for Σ is

$$\Sigma = \sum_{r=1} x_{r+1} \left(1 + \frac{\chi_r}{kT}\right).$$

This does injustice to the early x 's; for them, χ/kT is small and so the approximation gives the coefficient unity instead of $\pi^2/6$. However, these x 's are themselves very small, and the resulting error will not be serious. Again neglecting x_1 , we have then

$$\Sigma = 1 + \sum_{r=1} \frac{x_{r+1}\chi_r}{kT} = 1 + \frac{\bar{\chi}}{kT},$$

say, where $\bar{\chi}$ is the mean effective ionization potential. Since this will in general increase roughly proportionally to T (apart from complications arising from the factor $P/T^{5/2}$ in the dissociation formula), the value of Σ will be fairly steady. One after another, the successive stages of ionization will be dominant and control the value of χ .

The ratio of the fraction of r -fold ionized atoms to that of $(r-1)$ -fold ionized atoms is given by equation (21), and it is clear that $x_r > x_{r-1}$ so long as

$$\frac{0.332 \sigma_r T^{5/2} e^{-\chi_r/kT}}{q_r P_e} > 1.$$

(We have substituted for $(2\pi m)^{3/2} k^{5/2} h^{-3}$ its numerical value.) As r increases, χ_r increases, and the left-hand side of the inequality decreases. The stage of ionization most abundantly represented is thus the r' -fold stage, where r' is the greatest value of r for which

$$\frac{\chi_r}{kT} < \log \frac{0.332 \sigma_r T^{5/2}}{q_r P_e} \dots \dots \dots (33)$$

Contributions to $\Sigma x_{r+1} \chi_r$ will arise principally from values of r in the neighbourhood of this value.

As an example, take the typical stellar conditions used by Eddington :

$T = 5.64 \times 10^6$ degrees, $\rho = 0.0678$ grm.cm.⁻³, $M = 2.83$,
which give

$$P = 1.123 \times 10^{13} \text{ dynes.cm.}^{-2}$$

We may take this as giving also P_e . We then find that the relative abundance of the successive stages of ionization will increase so long as

$$\frac{\chi_r}{kT} < 2.3026 \log_{10} \frac{0.332 \times (5.64)^{5/2} \times 10^{15}}{1.123 \times 10^{13}} = 7.70.$$

For this temperature kT is 485 volts, and so the critical ionization potential is $485 \times 7.70 = 3730$ volts. If the atom in question possesses an ionization potential of this order we may adopt it for χ , and we have then

$$\Sigma = 1 + 7.70 = 8.70.$$

If, however, the atom does not possess an ionization potential of this order, we must take the next lowest one, and χ/kT will be somewhat lower. For example, let us suppose that the r -fold stage is the most abundant, and that χ_r differs considerably from the two neighbouring potentials χ_{r+1} and χ_{r-1} . It is then easily seen that x_{r-1} and x_{r+2} may be neglected in comparison with x_r and x_{r+1} , and *a fortiori* the fractions of less and more ionized atoms respectively. Hence χ reduces effectively to

$$x_r \chi_{r-1} + x_{r+1} \chi_r.$$

But now the fractions x_r and x_{r+1} comprise practically the whole number of atoms, and so $x_r + x_{r+1} = 1$. Hence

$$\bar{\chi} = \chi_{r-1} + x_{r+1}(\chi_r - \chi_{r-1}).$$

But $x_{r+1} \geq x_r$, and hence $1 \geq x_{r+1} \geq \frac{1}{2}$. Hence χ must lie between χ_r and $\frac{1}{2}(\chi_r + \chi_{r-1})$.

For iron* the L absorption limit is about 720 volts, the K-limit about 7100 volts. The ionization potentials for the removal of the corresponding L- or K- electrons after all the more loosely bound electrons have been detached will be considerably higher than these, but they will probably lie well on either side of the critical potential found above. Thus the iron atoms will be practically completely ionized as to their L-ring, but will mostly retain their K-ring†. The value of the correcting factor will be about $1 + 900/485 = 2.8$. On the other hand, for an element with an atomic number in the neighbourhood of 40 (Zr), the L-limit is about 2300 volts, the K-limit about 18,000 volts, and the value of the correcting factor would be about $1 + 2500/485 = 6.1$. In general it appears probable that a factor somewhat larger than Eddington's 2.70 will be required, though it will vary irregularly from place to place in the star.

Roughly speaking, the more nearly an element possesses an ionization potential approximating to the critical potential given by (33), the greater the absorption coefficient. For the greater is χ_r in relation to the critical potential, the more abundant are the $(r'-1)$ -fold ionized atoms which are chiefly effective in the absorption, and the increase in their number more than counterbalances the diminution in their mean absorbing power due to the restriction imposed by the higher χ_r on the region of the spectrum for which they are available.

This is not the occasion to examine in detail the successive ionization potentials of the various elements, and their relation to the absorption of radiation at high temperatures, but it is clear that it is only a question of ascertaining these in order to be able to determine with precision the mean absorption coefficient, on the hypotheses introduced.

§ 19. Summary.

The paper is concerned with the evaluation of the absolute values of optical absorption coefficients. The word "optical" is to be understood as referring to the outer levels of an atom, though for highly-ionized atoms the corresponding frequencies may lie in the X-ray region.

The absolute values of monochromatic optical absorption

* Bohr and Coster, *Zeit. für Phys.* xii. p. 350 (1923).

† Compare Eggert, *Phys. Zeit.* xx. p. 570 (1919); Seares, *Astrophys. Journ.* lv. p. 227 (1922).

coefficients for neutral or once-ionized atoms appear to be of the order of magnitude of 10^9 , (§ 1), but little is known concerning them either experimentally or theoretically. A method of calculating them is furnished by Einstein's discussion of the thermodynamic equilibrium subsisting between a gas and black radiation in an enclosure. This provides a relation between the absorption coefficient and the mean time of occupancy of an outer orbit, the order of magnitude of which is known experimentally. It is shown, however, that the relation involves the unknown theoretical width of the "monochromatic" line (§ 5), and is therefore not available for precise estimates. But it provides confirmation of the order of magnitude of the absorption coefficients (§ 6).

Einstein's method can be applied to any condition of equilibrium to determine a relation between the "reaction-velocities" of the opposing processes (§ 4). In §§ 8-11 it is so applied to obtain the relation between photo-electric ionization and the probability of electron-capture by an ion, considering the equilibrium subsisting between atoms, ions, electrons, and radiation in an enclosure. For strict thermodynamic equilibrium it is found necessary to assume that electron-capture can be stimulated by external radiation (§ 9). The relation found evaluates the absorption coefficient for the region of continuous absorption lying on the high-frequency side of the limit of an optical series, in terms of the capture-probability function.

It is shown that for small speeds the probability of capture must vary inversely as the square of the velocity (§ 12). In so far as this holds exactly, the absorption coefficient beyond the series limit will vary as the inverse square of the frequency (§ 14).

The capture law used by Eddington for the interior of a star, where the mean absorption coefficient is of the order of 40 and the frequencies are in the X-ray region, is an inverse square law. Applied to hydrogen, calcium, and mercury by means of the formulæ obtained in the paper, it furnishes absorption coefficients in the optical region for the continuous spectrum beyond a series limit which are in agreement with the estimates of the monochromatic absorption coefficients already mentioned (§ 13). This gives some confirmation of the inverse square law over a considerable range of velocities; it may be considered as linking up the physics of the interior of a star, the physics of stellar atmospheres, and the physics of the atom.

The mean life of a hydrogen atom in the 2-quantum state, under the conditions of a typical stellar atmosphere, is shown

to be about 10^{-8} second, as limited by the process of photo-electric ionization (§ 15).

The mean absorption coefficient for a highly-ionized gas at high temperatures is determined (§ 16) ; it differs from Eddington's formula by a factor depending on the relevant ionization potentials (§§ 17, 18). The order of magnitude of these is determined as a function of pressure and temperature, and it is shown, for example, that under typical conditions in the interior of a star, atoms of iron will have lost their L-electrons but will mostly retain their two K-electrons.

The validity of the method and of the resulting formulæ is shown to be entirely independent of the extent to which ionization occurs by collision (§§ 4, 17).

I am grateful for the many opportunities I have had of discussing the foregoing paper with Mr. R. H. Fowler.

12th November, 1923.

XIX. *Note on an important Property of the Auto-Transformer.* By W. H. INGRAM, *B.Sc.**

THERE are two methods of attacking the problem of the electrical transformer : the differential equation method, which goes back to Maxwell, and the "symbolic" method, due to Dr. Hopkinson †. The symbolic method presupposes simple sinusoidal potentials, fluxes, and currents (thus ignoring transients), but is applicable in cases where one or more of these quantities is not strictly sinusoidal by the simple fiction of "effective" circuit constants to give results to check with readings of wattmeters, etc., without regard to what the actual values of these constants are for the various Fourier components of the non-sinusoidal quantities in question. The symbolic method consists of a complex algebra of the relations among a system of radially-arranged vectors in a plane with reference to an associated coordinate system, the whole being conceived as steadily rotating, so that the projections of the said vectors on a reference-line in the plane give the sinusoidal variations in the quantities which the vectors represent. By neither

* Communicated by the Author.

† Given in a paper read before the Royal Society, March 10, 1887.

method, heretofore, has the transformer problem been solved in the sense of showing how all the electrical constants (effective or actual) of a transformer can be measured or calculated, or, as a matter of fact, any of them precisely, and it is the purpose of this note to show how all the electrical constants of a transformer may be *precisely* calculated on data from certain measurements and, moreover, for *any* condition of operation.

The data on a transformer essential to a precise calculation of its behaviour in operation are: its effective turns-ratio, effective winding resistances and leakage reactances, and excitation. All of these quantities are approximately determinable by well-known methods which give results sufficiently accurate for ordinary power circuits*, but it has been found that in circuits such as occur in telephone practice, where a transformer is often required at different times to operate under different impressed voltages and frequencies, the ordinary measurements of the quantities in question are insufficiently exact when used for predicting the behaviour of the transformer under abnormal conditions of excitation.

The crux of the problem lies in the handling of the core-losses, which may be thought of as occurring in a circuit linked to the working flux and of such impedance that the resistance part results in a power-loss corresponding to the hysteresis and eddy-current losses in the core, and such that the reactance part thereof consumes the wattless e.m.f. of excitation. If the coupling-ratio be taken as unity, such a system is the equivalent to the usual net† in which the core-losses are considered as taking place in a conductance and the magnetizing current as carried by a susceptance in a branch parallel to the conductance. The coupled-circuit equivalent, however, has an advantage of generality, being applicable in such cases as that of the auto-transformer, which admits of no equivalent conducting net.

A formula for the secondary-terminal potential of an auto-transformer is easily obtained on the assumption of the coupled excitation-circuit, and in the case of the step-down auto-transformer, or compensator, presents a novel property. Consider such a compensator having $n_1 + n_2$ primary and n_2 secondary effective turns and imagine the exciting circuit

* See Agnew and Silsbee, *Bull. of Bureau of Stds.*, vol. x. (1914).

† Cf. Russell, 'Alternating Currents,' vol. ii. chap. xii.; and Steinmetz, 'Alternating Current Phenomena,' chap. xvii.

to have an impedance Z_0 and to be linked by n_0 effective turns to the working flux. Let the impedances of the two windings be Z_1 and Z_2 , said impedances being made up of the effective resistances and leakage reactances associated with their respective windings. The usual magnetomotive-force, current, and electromotive-force requirements give :

$$\left. \begin{aligned} n_1 i_1 + n_2 i_2 &= n_0 i_0, \\ i_1 &= i_2 + i_a, \\ e_1/n_1 &= e_2/n_2, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (1)$$

and, as a definition of Z_0 :

$$i_0 = \frac{1}{Z_0} \frac{n_0}{n_1 + n_2} (e_1 + e_2), \quad . \quad . \quad . \quad . \quad (1a)$$

where e_1 and e_2 are the internal e.m.f.'s (that part of the applied voltage E_1 which cancels the counter e.m.f. produced by the working flux). From (1) and (1a) and the equations

$$\left. \begin{aligned} E_1 &= i_1 Z_1 + E_a + e_1 \\ E_a &= i_2 Z_2 + e_2 \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (2)$$

it is easy to derive the formula for the secondary voltage E_a :

$$E_a = \frac{n_2}{n_1 + n_2} E_1 - \frac{n_0(n_2 Z_1 - n_1 Z_2)}{(n_1 + n_2)^2} i_0 - \frac{n_2^2 Z_1 + n_1^2 Z_2}{(n_1 + n_2)^2} i_a, \quad (3)$$

an inspection of which shows that when $n_1 Z_2 = n_2 Z_1$, the secondary terminal potential of the compensator will be independent of the exciting current. The E 's and i 's are vectors and the Z 's operators*.

Now, it is possible to connect up a transformer as a compensator, and with suitable loads and applied voltages to have exactly the same currents circulating in the coils in one case as in the other. This is so because there is no restriction on the direction of i_2 (with reference to the coordinate system mentioned in the first paragraph, or to the flux vector) as there is for the current in the secondary of a transformer.

* The secondary terminal potential of a step-up auto-transformer is given by :

$$E_a = \frac{n_1 + n_2}{n_1} E_1 - \left(\frac{n_2^2 Z_1 + n_1^2 Z_2}{n_1^2} \right) i_a - \frac{n_0}{n_1} \frac{n_2}{n_1} Z_1 i_0.$$

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If we put $n_0=n_1$ for simplification and let $\rho=n_1/n_2$, the impedance Z_t of a transformer with a secondary load Z_s is easily found to be

$$Z_t = \frac{\rho^2(Z_s + Z_2)Z_0}{Z_0 + \rho^2(Z_s + Z_2)} + Z_1, \quad . \quad . \quad . \quad (4)$$

and, of course, is a measurable quantity. Impedances z' and z'' in series the coils n_1 and n_2 may be introduced when the coils are connected as an auto-transformer and the relation

$$n_1(Z_2 + z'') = n_2(Z_1 + z') \quad . \quad . \quad . \quad (5)$$

experimentally established by adjusting z' and z'' until the secondary terminal voltage of the auto-transformer remains invariant under changes in the exciting current, which changes may be produced by superimposing small voltaic current on the alternating, or closing and opening the circuit of a loop or more of conductor linking the core. The impedance of the auto-transformer Z_s with the impedances z' and z'' connected in and with load Z_a is given by :

$$Z_s = \frac{Z_0[(1 + \rho)^2 Z_a + \rho^2(Z_2 + z'') + (Z_1 + z')] + \rho^2 Z_a(Z_1 + z' + Z_2 + z'') + \rho^2(Z_1 + z')(Z_2 + z'')}{Z_0 + \rho^2(Z_2 + z'' + Z_a)}, \quad (6)$$

and may be measured.

The effective turns-ratio ρ may be obtained by a special test using (5) by letting z' and z'' be simple resistances, r' and r'' large enough so that, if either of a pair of values give the same ratio, either pair may be used to give ρ from the approximation $\rho = (R' + r')/(R'' + r'')$, where R' and R'' are the resistances of the coils n_1 and n_2 respectively as given by direct-current measurements. The equations (4), (5), and (6) are formally sufficient to give the remaining unknowns Z_1 , Z_2 , and Z_0 , but the latter must be really the same in all measurements, a condition which will obtain if the currents flowing in the coils are exactly the same. The load Z_a must be of such a magnitude that the current i_a will be equal to $(1 + n_2/n_1)i_2 + i_0$ (vectorially), where i_2 is the current in the transformer secondary during the measurement of Z_t and i_0 is the exciting current for the transformer primary for the operating voltage thereof, which also must be kept constant.

Solving for Z_0 and Z_1 (or Z_2) from (4) and (5) and substituting in (6) gives a cubic equation in Z_2 (or Z_1). If Z_0 is known to be comparatively large, as is the case in efficient transformers, (4) reduces to $Z_1 = \rho^2(Z_0 + Z_2) + Z_1$ approximately, and Z_1 and Z_2 may very easily be calculated using (5) and thereafter Z_0 calculated from (4).

A question which suggests itself is in regard to the effect of z' and z'' on the current wave-form and hence on the quantities to be measured. A qualitative answer to this problem may be obtainable when sufficient experimentation with the formulas of this note has been done, but at present it can only be said that when there is a comparatively large resistance in the generator circuit the current wave-form will be practically that of the voltage wave-form, and will be uninfluenced by small impedance variations in the transformer circuit.

Synopsis.

Voltage formulas are given for the auto-transformer and a method for measuring the leakage-fluxes, effective resistances, exciting impedance, and effective turns-ratio of a transformer.

Massachusetts Institute of Technology.

XX. The Emission of Secondary Electrons from Metals under Electronic Bombardment.

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IN the *Philosophical Magazine* for May 1923, Mr. E. W. B. Gill criticized our interpretation of the results of a series of experiments which we made in the course of an investigation of the effects of electron collisions with platinum and with hydrogen. Mr. Gill had recently performed some experiments with a view to investigating the emission of secondary electrons from nickel, but found that the apparatus he employed (a Marconi M. T. 5 thermionic valve) was unsuitable for obtaining information with regard to the critical voltage at which the secondary emission begins, or the maximum velocity with which the secondary electrons are emitted from the metal. His criticisms of the way in which we interpreted our results were based on the assumption

that the apparatus we had used suffered from defects similar to those of his own apparatus. We replied to this criticism in your issue of July 1923, pointing out that the difficulties experienced by Mr. Gill were not encountered by us because our apparatus and method of experiment were designed to render the disturbing effects sufficiently small to be negligible in comparison with the effect under investigation.

In his criticism Mr. Gill attributed the falling-off of the number of secondary electrons leaving our bombarded platinum plate while this was still about 5 volts negative to the grid, to inadequate shielding of the plate by the grid. We showed in our reply that this could not have been the case, and in the current number of your Magazine Mr. Gill withdraws his contention, but returns to the attack along other lines. The tone of his criticism suggests that Mr. Gill thinks we ought to have performed the investigation using grid potentials up to 600 volts, as he did. It is difficult to see what useful purpose would be served by employing hundreds of volts on the grid when investigating a critical potential known to be less than 15 volts, especially as it is to be anticipated that the relative importance of the disturbing effects in comparison with the effect under investigation is likely to increase with the employment of large voltages. In the course of his letter Mr. Gill states:—
 “Prof. Horton and Dr. Davies used only one value of V_G , and deduced from a bend in their curve that secondary emission commenced for a velocity of impact corresponding to a potential drop of about 10 volts.”

The description of our experiments (Proc. Roy. Soc. A, vol. xcvii. p. 23, 1920) gives no justification for the statement that we used only one value of V_G . It is clearly indicated that observations were taken with different arrangements of the various electric fields, and it is expressly stated that our difference of potential V_z (which controls V_G the difference of potential between the grid and the filament) was varied. Moreover, what we actually deduced from our curves was that an abrupt change in the rate of increase of the secondary current with increasing velocity of the primary stream commenced at an applied potential difference of between 10 and 11 volts, a result which we interpreted as supporting the view of other workers that the excitation of secondary emission (as distinct from reflexion of the primary electrons) required an applied potential difference between these limits. We explained that a correction

must be added to this applied potential difference to give the voltage equivalent of the velocity of impact of the primary electrons on the plate. The critical velocity of impact was that corresponding to a potential difference of about 13 volts.

Mr. Gill quotes one of our statements almost correctly. The statement is as follows :—

“The proof that the shielding action of the grid was almost perfect disposes of Mr. Gill’s contention that, because the authors made no allowance for an increase, with increasing plate potential, of the primary current to the plate at the expense of the primary current to the grid, their estimate of about 9 volts as the equivalent velocity of emission of the fastest secondary electrons is unreliable, and its agreement with the results of Lenard and others accidental.”

He goes on to remark, however :—

“The above statement of Prof. Horton and Dr. Davies appears to imply that as the plate potential is increased, none of the primary current to the grid is diverted to the plate, since they say that my contention that this occurs is disposed of.”

It will be seen that what we claim to have disposed of is Mr. Gill’s contention that our estimate of the velocity of emission of the fastest secondary electrons is unreliable. Our statement does not imply that as the plate potential is increased, none of the primary current to the grid is diverted to the plate ; but we interpret the smallness of the downward slope of the part K of the curve reproduced in our paper as showing that, when the plate was 9 volts positive to the grid, this effect was negligibly small compared with the decrease which had occurred in the secondary emission from the plate.

The estimate of 9 volts as the maximum velocity of emission of the secondary electrons could only be considered unreliable if it could be shown that the current-potential difference curves from which it was obtained were a distortion of the true relations between the plate current and the electric field near the plate, such as would be obtained if the screening of the plate by the grid were very inadequate. As, however, it has been established that in our experiments the screening of the plate by the grid was almost perfect, it follows that the last-mentioned relations are correctly represented in the curve. Thus, there can be no doubt that the electric field in the neighbourhood of the plate at the stage when the steeply sloping portion, H, joins the part

K, which is almost parallel to the potential difference axis, is that due to the 9 volts which is then applied between the grid and the plate. If this junction of the two parts of the curve does *not* give a measure of the maximum velocity of the secondary electrons, then, either (a) the bend of a certain length of the curve immediately preceding 9 volts is to be attributed entirely to the variation of the primary electron current to the plate, or (b) in the part K of the curve above 9 volts, the current due to the secondary electrons is not of negligible magnitude, so that this part of the curve, which is nearly parallel to the potential-difference axis, is not an indication of the total primary current to the plate.

Now with regard to (a), an inspection of the curve shows that no appreciable length of the bend of the curve immediately below the 9-volts' point could possibly be due entirely to the variation of the primary plate current with the electric intensity near the plate, unless the curve were a considerable distortion of the relation between these quantities; and this we have shown is not the case. *Thus the maximum velocity of emission of the secondary electrons is not less than that equivalent to about 9 volts.*

With regard to (b), it follows from Mr. Gill's argument that, since the measured current remained almost constant as the potential difference between the grid and plate was increased beyond 9 volts, the primary plate current must either have attained an almost constant value at 9 volts, or must increase more rapidly with increasing plate potential than the measured current does in this part of the curve. In the event of the latter alternative occurring, the measured current could only remain practically constant if the secondary current increased at the same rate as the primary plate current. Such an occurrence is extremely improbable, since it would mean that when the potential difference between the grid and the plate is increased beyond 9 volts, the current carried by the secondary electrons leaving the plate suddenly begins to increase, instead of continuing to decrease, with increase of the field tending to prevent electrons leaving the plate.

If the primary plate current has attained its saturation value when the potential difference between the grid and the plate has reached 9 volts, then, since the actual measured current is practically independent of the subsequent increases of plate potential, it follows that the current

due to the secondary electrons leaving the plate must have attained a value which is constant within the limits detectable in our investigation—that is to say, it must have become independent of the velocity of impact of the bombarding electrons or of the resulting potential difference opposing the motion of the electrons from the plate to the grid. This result is readily explained if this constant value of the secondary current is zero, whereas whatever the origin of the secondary current it is difficult to see how, if this current is at all comparable with the primary plate current, it can be sensibly independent of the two factors mentioned above. It therefore appears that *there is no appreciable number of secondary electrons leaving the plate with velocities greater than that corresponding to a potential difference of about 9 volts.*

Thus the most reasonable interpretation of the junction of the parts H and K of the curve which occurs at about 9 volts is that secondary emission practically ceases at this stage because the velocity of emission of the fastest secondary electrons from platinum corresponds to a potential difference of this value.

We therefore maintain that our proof that the shielding action of the grid in our experiments was almost perfect has disposed of Mr. Gill's contention that our estimate of the velocity of emission of the fastest secondary electrons is unreliable. This estimate—like the other conclusions we drew from this series of experiments—is in general agreement with all the more recent work on the subject*.

* R. A. Millikan and I. G. Barber, Proc. Nat. Acad. Sci. vol. vii. p. 13 (1921); I. G. Barber, Phys. Rev. vol. xvii. p. 322 (1921); H. E. Farnsworth, Proc. Nat. Acad. Sci. vol. viii. p. 251 (1922), and Phys. Rev. vol. xx. p. 358 (1922); L. E. McAllister, Phys. Rev. vol. xxi. p. 122 (1923).

Royal Holloway College,
Englefield Green.
Nov. 10th, 1923.

Yours faithfully,
F. HORTON,
A. C. DAVIES.

XXI. *Notices respecting New Books.*

Life Movements in Plants. By Sir JAGADIS CHUNDER BOSE, Longmans, Green & Co., 1913. (Transactions Bose Institute. vols. iii. & iv., 1920, 1921.) 20s. net.

THIS volume continues the lines of inquiry pursued in the two volumes on *Life Movements in Plants* by the same author published in 1915 and 1919. The present work contains accounts of investigations on geotropism, on dia-heliotropic attitude of leaves as regulated by transmitted nervous impulse, on assimilatory and dissimilatory changes under light, on new methods of recording the effects of protoplasmic changes under stimulus, and also of various methods and appliances for detection of the two fundamental reactions to which all plant movements are due. The important work done by Sir J. C. Bose is well known. This new series of researches is of great value, and will command the attention of all those who are concerned with the application of physical methods to biological phenomena.

Dynamics. By HORACE LAMB, Sc.D., LL.D., F.R.S. 2nd Edition. (Pp. xi+351, with 93 figures.) (Cambridge: at the University Press, 1923. Price 12s. 6d. net.)

THE first edition of this well-known text-book was published in 1914. It is a tribute to its excellence that in the new edition no alterations have been found necessary beyond the correction of a few errors, chiefly in the examples, and the re-writing of a few pages. Detailed notice of this edition is therefore unnecessary. It is worthy of mention that the price for the new edition has been reduced from 17s. 6d. net to 12s. 6d. net. It is very desirable that the price of books which are suitable for extensive use as text-books should be kept as low as possible, and it is to be hoped that the substantial reduction in the price of the present edition will make it accessible to a much greater number of students.

The Properties of Matter. By BASIL C. McEWEN, M.C., B.Sc. Professor of Science and Vice-Principal of His Exalted Highness The Nizam's College, Hyderabad, India. (Pp. vii+316, with 137 figures.) (London: Longmans, Green & Co., 1923. Price 10s. 6d. net.)

THE majority of text-books dealing with the Properties of Matter commence with a study of matter in the solid state and then proceed to the consideration of liquids and gases. In this way matter in its most complex form is studied first. In the present work the reverse order is followed, and this procedure has

much to recommend it. The standard is that of the B.A. and B.Sc. pass degrees. A noteworthy feature of the book is that, in addition to the theory of the subject, a number of experiments are described which the student can perform himself, and which will help to give him a better appreciation of the subject. It is advisable in this as in other branches of physics, that the practical and theoretical study should proceed together.

One peculiarity which strikes us in the treatment is that, although a chapter is devoted to the first law of thermodynamics no mention is made of the second law, which is, nevertheless, applied without explanation to such matters as the change of boiling and freezing points with pressure. We would suggest that in a second edition a short account of the second law should be incorporated.

The treatment of the various subjects touched upon follows conventional lines. Only an elementary knowledge of mathematics is assumed, and results whose derivation would require a more extensive knowledge, such as the rate of fall of a small sphere in viscous fluid, are given without proof. The text-book can be recommended for an elementary and comprehensive treatment of the properties of matter as far as the standard required for a University pass degree.

L'Evolution des Etoiles. By JEAN BOSLER, Director of the Marseilles Observatory. (Pp. 103, with 19 figures.) (Paris: Les Presses Universitaires de France, 1923. 10 f. net.)

THIS volume contains a concise and readable account of our present state of knowledge on the subject of the evolution of stars. Much of the original work which is summarised in it has only been published within the last few years, and it is valuable to have it collected together and arranged in logical sequence in such a volume as the present.

The classification of stars by their spectra is dealt with first. It was the progressive sequence into which stellar spectra could be classified which provided the basis for the initial theories of stellar evolution. For a time there were two rival theories: the one requiring an order of evolution commencing with the blue stars and proceeding through those of solar type to the red stars; the other required a two-branched order, commencing with red stars of low density and proceeding with rising temperature to blue stars, whence the sequence continued with decreasing temperature to red stars of high density. In this connexion the various methods by which the temperatures of stars have been determined are described.

An account is then given of the recent work of Saha, which has had such remarkable success in explaining the main features of stellar spectra, as due to ionization as a function of temperature and pressure. From a consideration of the appearance and disappearance of various lines, the approximate temperatures of

each type can be determined: these temperatures agree reasonably well with those obtained by observation.

The giant and dwarf theory of stars is led up to by a consideration of the spectroscopic method of determining stellar parallaxes, and of the results so obtained for the absolute luminosities of stars. It is shown that red stars may be divided into two groups of high and low luminosity, and that there are no blue stars of low intrinsic luminosity. An account of Russell's theory of evolution is then given. The relationship of this theory to the masses of the stars is considered, and it is shown that equipartition of energy obtains approximately for stars of different mass.

The general course of evolution having thus been indicated by the results of observation, the theoretical discussion of the same problem follows naturally. A fairly detailed account of the theory of radiative equilibrium is given. This theory, applied to giant stars, has had remarkable success in explaining the results of observation, and has also been successful in providing a general explanation of the phenomena shown by dwarf stars. It accounts also for the fact that the masses of stars are compressed within somewhat narrow limits; the temperature of stars of very small mass will never increase sufficiently for them to become visible, whilst very large masses would be blown asunder by the pressure of radiation.

Finally, the problem of the origin of the heat of the stars is considered.

Although the treatment in general is accurate and remarkably clear, there are one or two statements which are somewhat misleading. On p. 29, the agreement between the observed and calculated diameters of Betelgeuse is quoted as evidence that the stars radiate like black bodies. This agreement, of course, affords no evidence in the case of dwarf stars, which certainly do not radiate like black bodies. On p. 50, the remarks in reference to the relative numbers of stellar parallaxes determined by the trigonometrical and the spectroscopic methods do not state the case fairly. The spectroscopic results are based entirely upon the trigonometrical; moreover, the former for certain statistical purposes are of comparatively little value owing to the systematic dependence on the masses of the stars which has recently been pointed out. No mention of this dependence is made.

The New Physics: Lectures for Laymen and Others. By ARTHUR HAAS, Ph.D., Professor of Physics in the University of Leipzig. Translated by R. W. LAWSON, D.Sc. (Pp. xi+165, with 7 figures.) (London: Methuen & Co., 1923. Price 6s. net.)

Recent Developments in Atomic Theory. By LEO GRAETZ, Professor of Physics in the University of Munich. Translated by GUY BARR, B.A., D.Sc. (Pp. xi+174, with 39 figures.) (London: Methuen & Co., 1923. Price 9s. net.)

THESE two volumes both deal in a readable, non-technical manner

with some of the more important of the many recent striking developments of physics. The first one covers the wider ground. Commencing with an account of Maxwell's electromagnetic theory of light, a chapter on molecular statistics follows. These two lead naturally to the extension of Maxwell's theory by Lorentz, in his electron theory. The consideration of the structure of matter and of the quantum theory follow. The application of the latter has enabled the electron theory to be extended to cases in which the laws of classical mechanics failed to provide a satisfactory explanation. In particular, as developed by Bohr and others, it has enabled the spectrum of hydrogen to be accounted for, the fine structure of spectral lines and the arrangement of the elements into a periodic system. These matters are all dealt with in a lucid manner. The closing chapter deals with the theory of relativity, which in the hands of Einstein has completed the work of Maxwell and Lorentz, and provided an explanation of the phenomena of gravitation. The volume thus contains in brief compass an account of the most important developments of physics of recent years, written in a simple style suitable for the average intelligent layman.

The second volume deals more particularly with the recent work which has led to our present knowledge of the structure of the atom. Its publication has followed closely upon Professor Rutherford's presidential address at the last meeting of the British Association. The broadcasting of that address has stimulated many laymen with a desire to obtain further information with regard to this subject, in the development of which Rutherford has taken such an important part. This volume can confidently be recommended for this purpose. It starts with an account of the atomic theory in chemistry and in physics, and the use of statistical methods for the kinetic theory of gases. An account of ions in electrolysis leads to the conception of the atom of electricity, and so to the electron, and the phenomena of electrical discharges through gases. An account of radioactive phenomena follows, including Wilson's work which suggested Rutherford's theory of the atom. This is considered in conjunction with Aston's work on isotopes. Further support is given to the theory by X-ray spectra and the work of Moseley and others. An account then follows of line spectra and Bohr's model of the atom and of the extensive developments which have followed upon the application of the quantum theory. It thus provides a very complete but at the same time easily intelligible account of the present state of knowledge in this important branch of physics.

In conclusion, it may be added that the translators have in each case performed their task admirably.

XXII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xlv. p. 1026.]

November 7th, 1923.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

THE following communication was read:—

‘The Igneous Rocks of the Tortworth Inlier.’ By Prof. Sidney Hugh Reynolds, M.A., Sc.D., F.G.S.

The igneous rocks of the Tortworth Inlier were described by Prof. C. Lloyd Morgan and the author in a paper published in the *Quarterly Journal of this Society* in 1901 (vol. lvii. p. 267). The present paper contains information which has become available since the publication of that just cited. The igneous rocks occur in two bands, the upper of which is associated with calcareous tuffs containing Silurian fossils and is doubtless lava. The lower band was also regarded as a lava in 1901, but it now seems probable that it is intrusive. The rocks of the two bands, though showing well-marked differences, have several features in common. In each case the feldspars, although doubtless originally labradorite, are now wholly or partly in the condition of albite or oligoclase. In each case pyroxene is present only in the form of very small crystals, is relatively scanty, and predominantly rhombic. The rocks of the lower band are characterized by the presence of pseudomorphs after olivine, and may be grouped as olivine-enstatite-basalts.

Those of the upper band are devoid of olivine, and consist of pyroxene-andesite. They are characterized by the presence of highly corroded xenocrysts of quartz and feldspar, and by the occurrence of variolitic and glassy patches in the ground-mass.

November 21st.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

The following communication was read:—

‘The Development of the Severn Valley in the Neighbourhood of Iron-Bridge and Bridgnorth.’ By Leonard Johnston Wills, M.A., Ph.D., F.G.S.; with a Section on the Upper Worfe Valley, in collaboration with Ernest Edward Leslie Dixon, B.Sc., F.G.S.

The investigation of the Iron-Bridge Gorge and the surrounding country was undertaken with the view of finding detailed evidence for or against the hypothesis of the origin of the gorge as a Glacial overflow-valley. This hypothesis was put forward independently by Charles Lapworth¹ and F. W. Harmer.² Its correctness has been borne out by the detailed evidence now presented.

¹ *Proc. Geol. Assoc.* vol. xv (1898) p. 425.

² *Q. J. G. S.* vol. lxiii (1907) pp. 477-81.

The area investigated is roughly delimited by the following localities:—Much Wenlock, Buildwas, Oakengates, Shifnal, Worfield, Hampton Loade, Morville. It can be subdivided physiographically into

- (a) The Buildwas area, a part of the Shropshire plain.
- (b) The Barrow-Broseley and Madeley-Shifnal plateau, bounded on the north-west by Wenlock and Benthall Edges, and the Wrekin; it stretches as a main watershed, except at Iron-Bridge, north-eastwards towards Shifnal and Newport (Salop). This plateau was the pre-Glacial watershed between the Dee-Mersey drainage and the Worfe, which was then an important feeder of the Worcestershire Stour.
- (c) The Worfe Vale, a mature valley.
- (d) The Iron-Bridge Gorge, and its less gorge-like continuation as the Severn Valley by Bridgnorth.

Detailed mapping of the drifts has shown, first, that the Buildwas area was as deeply eroded as now in pre-Glacial times; and, secondly, that a belief in the existence of the Iron-Bridge Gorge at that time is incompatible with the distribution of the drifts on the plateau above Iron-Bridge, with the youthful features of the gorge, and with the absence of Glacial deposits in it. Everything points to the gorge being of late-Glacial origin, and to the Worfe Vale having been formerly the main drainage-line on the south-east side of the plateau, which then formed an unbroken watershed.

Practically the whole district was under ice at the maximum of the north-western or Irish-Sea glaciation. When retreat began, the ice-sheet separated into two lobes that remained confluent in the north. The lobe north-west of the pre-Glacial watershed was pressed counter-drainage against it. Glacial lakes were thus formed. The other lobe, on the south-east side, persisted longer in the low ground of the Worfe Vale. Marginal drainage was of special importance here, being reinforced by overflows from the lakes across the divide.

Various stages in the retreat are sketched out, and their relation to the drift-outcrops and to the former lines of drainage is shown; it is also shown how the waters of the Glacial lakes, west and north of the watershed, escaped at different times over different cols.

One of these overflows is of especial importance in connexion with the origin of the Iron-Bridge Gorge: namely, the Lightmoor overflow, about a mile north of Iron-Bridge. This appears to have drained a lake in Coalbrookdale, and to have operated before the Iron-Bridge overflow began. It is necessary to postulate a slight re-advance of the ice to close this overflow, and thus raise the level of the lake until it flowed out over a higher col at Iron-Bridge. Evidence for this re-advance is given. Reasons are adduced for the immediate rapid erosion of the upper part of the Iron-Bridge Gorge to a level too low to allow the Lightmoor overflow to operate a second time on the renewed retreat of the ice.

Up to about this stage, the Worfe and its tributaries (one of which now became the Iron-Bridge Gorge) had been engaged in

clearing the drift out of their valleys, and in reducing the thalweg of the trunk river to a base-level. Hereafter deposition of the 'Main' Terrace of the Severn and of the terrace-like gravels of the Worfe commenced. An important overflow at Oakengates brought water from another lake on the northern side of the watershed at this stage. Some of the gravels of the Mad Brook, the Worfe, and the Wesley Brooks can be correlated with this overflow.

As the ice retreated farther, the Coalbrookdale Lake was so enlarged that it covered the Buildwas area. Sands and gravels were deposited in the lake (the Buildwas Sands). The level of the lake fell to about 300 feet O.D. as the outlet was lowered; but there is evidence that it remained at about this level for a long time, probably on account of the graded state of the Severn Valley below Iron-Bridge, of which we have evidence in the Main Terrace. This terrace can be traced right down the Severn, although evidence for this is not brought forward here. Its connexion with the north-western or Irish-Sea glaciation will, however, be important in studying the relation of the terraces (not only of the Severn, but of other rivers) to the Glacial Episodes.

Long after the initiation of the Iron-Bridge Gorge, ice still covered the upper Worfe Valley. Retreat-stages here have been made out largely through the collaboration of Mr. E. E. L. Dixon. When the ice retired to the north of the watershed hereabouts, Glacial Lake Newport came into being, and subsequently united with the Buildwas Lake on the retreat of the ice-front from the foot of the Wrekin. The outflow at Iron-Bridge thus increased, although the united lakes maintained the 300-foot level, mentioned above, for some time. The subsequent rejuvenation of the Severn below Iron-Bridge was probably brought about chiefly by an elevation of the whole land relative to the sea. Stages in this rejuvenation are marked by terraces.

In the Bridgnorth area the terraces are as follows:—

*Approximate height in feet of the
terrace-surface above the present
flood-plain of the Severn.*

Hoads Park-Eardington Terrace	150 to 125
Main Terrace.....	120 to 100
Upper Danesford Terrace	70 to 60
Lower Danesford Terrace	35 to 30

So far, only the Lower Danesford Terrace has been recognized both above and below the Iron-Bridge Gorge.

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XXIII. *Statistical Equilibrium with Special Reference to the Mechanism of Ionization by Electronic Impacts.* By R. H. FOWLER, Fellow and Lecturer in Trinity College, Cambridge*.

§ 1. *Introduction.*

IN a number of recent papers, the earliest by Klein and Rosseland †, it has been shown that the study of specific atomic processes of energy exchange, in quite general terms, is likely to prove exceedingly fruitful. The underlying idea may be expounded as follows. The laws of thermodynamics and of statistical mechanics (modified to include the modern quantum theory) specify certain characteristics of the equilibrium conditions of matter. The former are believed to be of universal applicability, the latter hardly extend as yet much beyond the distribution laws of dilute gaseous assemblies. In their proper regions, however, we believe these laws to be of general validity, and they then form a framework to which all detailed processes of energy exchange must conform. We believe in fact that these laws are true whatever the mechanism of such processes may be. It seems quite certain that, for example, the law of distribution of the velocities of free electrons must be the same in any enclosure in thermodynamic equilibrium. Accepting it, we can consider various assemblies at the same temperature, in

* Communicated by the Author.

† Klein & Rosseland, *Zeit. für Phys.* iv. p. 46 (1921).

which different processes of exchange are going on, or the same processes at rates which can be altered relatively to one another by altering the concentrations. Since the resulting distribution laws must be the same in form, it follows that any one process of exchange acting in a particular direction must be invariably accompanied by an analogous reverse process. The pair must be capable in combination of maintaining by themselves the regular laws. This combined action can never require the assistance of any other process, unless such process can be and is its invariable accompaniment, and then in fact forms part of one group of processes which may conveniently be referred to as a *unit mechanism*. From the fact that each unit mechanism must maintain by itself the regular distribution laws for all temperatures, we can deduce important consequences as to the relative frequencies of occurrence of the constituent processes that compose the unit. In the first instance such a study may even lead to the recognition of a type of process not hitherto suspected to be of importance.

The unit mechanism studied by Klein and Rosseland is based on the well-known inelastic collisions between electrons with more than a certain energy and atoms, whereby an electron in the atom is transferred from one stationary orbit to another of greater energy, apparently without the emission or absorption of any radiation. These are collisions of the first kind. They deduce the existence of "super-elastic" collisions or collisions of the second kind, which form the associated reverse process necessary to complete the mechanism. These consist in the collision of an electron with an excited atom in which the atom returns to normal and the electron goes off with all the superfluous energy in the kinetic form. These ideas have been further developed by Franck* and others, and have already proved of great value in the qualitative interpretation of a variety of phenomena. We shall find it convenient to reformulate the discussion of this mechanism on somewhat broader lines as an introduction to the discussion of another unit mechanism which forms the main theme of this paper.

More recently a second unit mechanism has been studied in detail, of which one constituent is the photoelectric effect. The associated reverse process is the capture of an electron by an ion through the emission of radiation in the encounter.

* Franck, *Zeit. für Phys.* ix. p. 259 (1922); Cario, *ibid.* x. p. 185 (1922); Cario & Franck, *ibid.* xi. p. 161 (1922), xvii. p. 202 (1923).

This has been studied independently by Kramers* and Milne†—the one developing the theory in connexion with the continuous X-ray spectrum emitted by the anticathode of a vacuum tube, and the other with optical absorption coefficients and with Eddington's theory of the interior of giant stars. It should not be overlooked that all these discussions derive from Einstein's classical theory of Planck's Law of Temperature Radiation‡. The processes of which he treats are the absorption and emission of the optical spectra of atoms, which together form a third unit mechanism.

It is the main purpose of this paper to examine a fourth unit mechanism based on the process of ionization by collision, in particular by electronic impact§. The associated reverse process must clearly be a three-body encounter, which results in the binding of two of the constituents to form a single atom or molecule, the superfluous energy being carried off by the third body. We shall find that the frequencies of these processes can be simply formulated, and that relations hold between the frequencies which are closely analogous to those given by Klein and Rosseland for inelastic and "superelastic" impacts. In order to make practical applications of the theory it is necessary to know from independent evidence the form of the frequency of one of the processes. This is provided to some extent by β -ray phenomena for the frequency of the process of ionization.

It is then possible to examine roughly the relative importance of radiative and radiationless captures and ionizations in controlling the equilibrium of gaseous assemblies at high temperatures, in particular in the reversing layers of stars. We find that for typical reversing layer conditions (pressure of 10^{-4} atmosphere) the radiationless (collision) captures are just negligible. They may, however, be expected to become of importance somewhat greater than the radiative captures at a pressure of about 1 atmosphere.

* Kramers, *Phil. Mag.* xlv. p. 836 (1923).

† Milne, *Phil. Mag.* xlvii. p. 209 (1924).

‡ Einstein, *Phys. Zeit.* xviii. p. 121 (1917).

§ After this paper had been written, a very interesting paper by Becker, *Zeit. für Phys.* xviii. p. 325, published 17 Oct. 1923, came to hand in which the same process is discussed. The author obtains my formula (A) of § 3, but omits to discuss the atomic balance. He thus does not give (B) or observe that probably the correct result is (C), and he does not discuss the relative importance of radiative and radiationless ionizations and captures. The author deals also with radiative captures in the manner of Milne, and with other important points in the theory of statistical equilibrium. [Note added to proof. The recent elegant work of Pauli, *Zeit. für Phys.* xviii. p. 272 (1923) on the equilibrium between radiation and free electrons belongs to the same order of ideas.]

This result may prove to be of some interest, for it suggests a further quantitative study of the disturbance of the thermodynamic equilibrium of the reversing layer under the influence of a flux of radiation of a temperature greater than its own. It is possible that the next step in the development of Saha's theory lies in this direction, as has already been suggested by H. N. Russell and K. T. Compton.

No attempt is made in this paper to follow up this mechanism into its wider ramifications. They must clearly be of importance in many phenomena. The investigation of the nature of dissociative steady states in the presence of a temperature gradient is as yet an untouched field. It must be tractable at least formally in terms of the frequency coefficients analogous to those whose relations we establish here. But the most interesting field for immediate application would seem to be Rutherford's results on the capture and loss of electrons by α -particles. This will be dealt with in another paper, which will be published shortly.

§ 2. *Klein and Rosseland's Results.*

The frequency of collisions either of the first or second kind (inelastic or superelastic) can be expressed in terms of a certain coefficient, of the dimensions of an area, which is a function solely of the atom and the relative velocity and line of impact of the electron hitting it. This coefficient, which represents the chance of a successful collision, may also depend in an individual collision on the orientation of the axis of the atom relative to the line of impact and on the exact position of the electron in its orbit. The average coefficient, however, which in general is all we shall be concerned with, is obtained by integration over all values of these variables, which are therefore no longer effective. It is of some importance for general applications to secure that all the atomic functions, which are introduced as frequency coefficients, genuinely are atomic functions, and do not depend on extraneous parameters.

Let

$$\mu(\epsilon)d\epsilon = \frac{4\pi\eta}{(2\pi kT)^{3/2}} e^{-\epsilon/kT} (2\epsilon)^{1/2} d\epsilon \quad \dots \quad (\text{Maxwell's Law}) \quad (1)$$

be the number of electrons per unit volume whose energies lie between ϵ and $\epsilon + d\epsilon$. These we shall call ϵ -electrons. The total electron density is η , T is the absolute temperature, and k is Boltzmann's constant. If x_1 is the density of any type of atom, which for the moment we suppose fixed in

space or of infinite mass, then the number of collisions per unit volume per second between atoms and ϵ -electrons in which the line of impact lies at a distance between p and $p+dp$ from the atomic nucleus is

$$x_1 \cdot 2\pi p dp \cdot \left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon) d\epsilon. \quad (2)$$

If $\Sigma_1^2(p, \epsilon)$ is the probability that such a collision is successful in exciting the atom (from state 1 to state 2 say), the number of such successful collisions is

$$x_1 \cdot 2\pi p dp \cdot \Sigma_1^2(p, \epsilon) \left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon) d\epsilon. \quad (3)$$

Writing

$$S_1^2(\epsilon) = 2\pi \int_0^\infty p \Sigma_1^2(p, \epsilon) dp, \quad (4)$$

we find the total number of successful collisions of the first kind by ϵ -electrons to be

$$x_1 S_1^2(\epsilon) \left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon) d\epsilon. \quad (5)$$

This expression is only relevant when $\epsilon \geq \epsilon_{12}$, where ϵ_{12} is the extra energy required by the atom in state 2 compared with state 1. When $\epsilon < \epsilon_{12}$, $S_1^2(\epsilon) \equiv 0$. In an exactly similar manner the total number of successful collisions of the second kind by ϵ -electrons can be written

$$x_2 S_2^1(\epsilon) \left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon) d\epsilon, \quad (6)$$

in which x_2 is the density of atoms in state 2. These collisions can be effective for any value of ϵ . In the present formulation $S_1^2(\epsilon)$ and $S_2^1(\epsilon)$ have a purely atomic significance; they may be called the mean effective collision areas of the atom for ϵ -electrons. Expressions (5) and (6) differ from those of Klein and Rosseland in the inessential factor $(2\epsilon/m)^{1/2}$, but Klein and Rosseland's coefficients have no very simple meaning.

By considering the conditions for the preservation of Maxwell's Law for the velocity distribution of the electrons, a fundamental relation has been established between $S_1^2(\epsilon)$ and $S_2^1(\epsilon)$. The concentrations x_2 and x_1 are connected according to the ordinary laws of statistical mechanics by the relation

$$x_2/x_1 = (g_2/g_1) e^{-\epsilon_{12}/kT}, \quad (7)$$

in which g_1 and g_2 are the statistical weights of these states.

The consequent relation between $S_1^2(\epsilon)$ and $S_2^1(\epsilon)$ in the present notation is

$$q_1(\epsilon + \epsilon_{12})S_1^2(\epsilon + \epsilon_{12}) = q_2\epsilon S_2^1(\epsilon), \quad . . . \quad (8)$$

which holds for all values of ϵ . Relation (8) guarantees the preservation of the electron distribution laws for all values of T . It also of course guarantees the preservation of (7). For the rate of destruction of atoms in state 1 by this mechanism is

$$x_1 \int_{\epsilon_{12}}^{\infty} S_1^2(\epsilon) \left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon) d\epsilon,$$

and the rate of production

$$x_2 \int_0^{\infty} S_2^1(\epsilon) \left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon) d\epsilon.$$

Using (1) and (7) we see that these rates will balance when

$$q_1 \int_0^{\infty} (\epsilon + \epsilon_{12}) S_1^2(\epsilon + \epsilon_{12}) e^{-\epsilon/kT} d\epsilon = q_2 \int_0^{\infty} \epsilon S_2^1(\epsilon) e^{-\epsilon/kT} d\epsilon, \quad (9)$$

which is satisfied for all values of T in virtue of (8). It is, however, of interest to observe that (8) can be deduced directly from the fact that (9) must hold for all T . Equation (9) is of the general form

$$\int_0^{\infty} f(\epsilon) e^{-\epsilon/kT} d\epsilon = 0, \quad (\text{all } T). \quad . . . \quad (10)$$

The necessary deduction is ensured by the following

Lemma.—If $f(\epsilon)$ is a continuous function of ϵ for $\epsilon \geq 0$ and

$$\int_0^{\infty} f(\epsilon) e^{-\epsilon/kT} d\epsilon = 0, \quad (\text{all } T),$$

then

$$f(\epsilon) = 0, \quad (\text{all } \epsilon \geq 0).$$

This lemma is a direct consequence of Fourier's integral theorem. There is no physical reason to question the applicability of the conditions of the lemma to the function $f(\epsilon)$ derived from the atomic collision areas in (9).

One might naturally hope to be able to deduce in the same way that a relation of the form (8) will hold for the frequencies of every possible switch by collision in an atom with n levels. It appears, however, that no such deduction can be drawn from the general premises of this paper. An atom with n possible levels has $\frac{1}{2}n(n-1)$ possible switches, all of which we must regard as forming one unit mechanism.

In an assembly in equilibrium at a given temperature we have no means of varying the relative frequencies of the constituent processes as we can vary the relative frequencies of processes of different unit mechanisms by changes of concentration. They must be discussed together and analysed, so far as they can be, only by variation of the temperature.

A detailed presentation of the case $n=3$ is instructive. There are three pairs of to and fro switches to consider. Sufficiently slow ϵ -electrons are created only by collisions of the first kind at a rate

$$\begin{aligned} & x_1 S_1^2(\epsilon + \epsilon_{12}) \left\{ \frac{2(\epsilon + \epsilon_{12})}{m} \right\}^{1/2} \mu(\epsilon + \epsilon_{12}) d\epsilon \\ & + x_1 S_1^3(\epsilon + \epsilon_{13}) \left\{ \frac{2(\epsilon + \epsilon_{13})}{m} \right\}^{1/2} \mu(\epsilon + \epsilon_{13}) d\epsilon \\ & + x_2 S_2^3(\epsilon + \epsilon_{23}) \left\{ \frac{2(\epsilon + \epsilon_{23})}{m} \right\}^{1/2} \mu(\epsilon + \epsilon_{23}) d\epsilon. \quad (11) \end{aligned}$$

They are destroyed only by collisions of the second kind at a rate

$$\{x_2 S_2^1(\epsilon) + x_3 S_3^1(\epsilon) + x_3 S_3^2(\epsilon)\} \left(\frac{2\epsilon}{m} \right)^{1/2} \mu(\epsilon) d\epsilon. \quad (12)$$

The condition for the preservation of the regular laws of equilibrium can be written

$$e^{-\epsilon_{12}/kT} F_1^2(\epsilon) + e^{-\epsilon_{13}/kT} \{F_1^3(\epsilon) + F_2^3(\epsilon)\} = 0, \quad (\text{all } T), \quad (13)$$

an equation valid only when ϵ is less than the least of ϵ_{12} , ϵ_{13} , and ϵ_{23} . The notation should be sufficiently clear, on remarking that, for example, $F_1^2(\epsilon) = 0$ would be equivalent to (8). When ϵ is unrestricted the first terms in (11) and (12) continue to give the numbers of ϵ -electrons created by the switch $1 \rightarrow 2$ and destroyed by $2 \rightarrow 1$. There are now in addition

$$x_1 S_1^2(\epsilon) \left\{ \frac{2\epsilon}{m} \right\}^{1/2} \mu(\epsilon) d\epsilon$$

ϵ -electrons destroyed by the switch $1 \rightarrow 2$, and

$$x_2 S_2^1(\epsilon - \epsilon_{12}) \left\{ \frac{2(\epsilon - \epsilon_{12})}{m} \right\}^{1/2} \mu(\epsilon) d\epsilon$$

ϵ -electrons created by the switch $2 \rightarrow 1$. There are similar terms for the other two switches. If we make the convention that in all cases $F_r^s(x) = 0$, when $x < 0$, the new terms above can be accounted for by adding the term $-F_1^2(\epsilon - \epsilon_{12})$ to (13). The complete form of (13) is therefore

$$\begin{aligned} & -\{F_1^2(\epsilon - \epsilon_{12}) + F_1^3(\epsilon - \epsilon_{13})\} + e^{-\epsilon_{12}/kT} \{F_1^2(\epsilon) - F_2^3(\epsilon - \epsilon_{23})\} \\ & + e^{-\epsilon_{13}/kT} \{F_1^3(\epsilon) + F_2^3(\epsilon)\}, \quad (\text{all } T, \epsilon). \quad (14) \end{aligned}$$

This is equivalent to the three equations

$$F_1^2(\epsilon - \epsilon_{12}) + F_1^3(\epsilon - \epsilon_{13}) = 0,$$

$$F_1^2(\epsilon) - F_2^3(\epsilon - \epsilon_{23}) = 0,$$

$$F_1^3(\epsilon) + F_2^3(\epsilon) = 0,$$

of which two only are independent. They reduce to

$$F_1^2(\epsilon) = F_2^3(\epsilon - \epsilon_{23}) = -F_1^3(\epsilon - \epsilon_{23}) \dots (15)$$

We can infer that equation (8), $F_1^2(\epsilon) = 0$, still holds for $\epsilon < \epsilon_{23}$, but we can infer nothing more as to the vanishing of the F 's. The assumption of only two stationary states is equivalent to making ϵ_{23} infinite. It may be noted in passing that if we rule out entirely the possibility of switches by collisions of type $2 \rightarrow 3$ and $3 \rightarrow 2$, then $F_2^3 \equiv 0$, and we can infer that $F_1^2(\epsilon) = 0$ and $F_1^3(\epsilon) = 0$ for all ϵ . This is the expected inference generalizing (8). But it can only be made when by an artificial limitation we have ruled out the possibility of the cyclic process $1 \rightarrow 2$, $2 \rightarrow 3$, $3 \rightarrow 1$. I cannot find any convincing *a priori* reason to believe that such cycles are not permissible.

It remains to determine the conditions under which the distribution of atoms between the states is preserved. For state 1 this can be written

$$e^{-\epsilon_{12}/kT} \int_0^\infty F_1^2(\epsilon) e^{-\epsilon/kT} d\epsilon + e^{-\epsilon_{13}/kT} \int_0^\infty F_1^3(\epsilon) e^{-\epsilon/kT} d\epsilon = 0,$$

and finally reduced to the form

$$\int_0^\infty \{F_1^2(\epsilon) + F_1^3(\epsilon - \epsilon_{23})\} e^{-\epsilon/kT} d\epsilon = 0, \text{ (all } T). \dots (16)$$

Condition (16) is equivalent to one of the equations (15) and gives us nothing new. In the same way for states 2 and 3, we get

$$\int_0^\infty \{-F_1^2(\epsilon) + F_2^3(\epsilon - \epsilon_{23})\} e^{-\epsilon/kT} d\epsilon = 0, \text{ (all } T),$$

$$\int_0^\infty \{F_1^3(\epsilon) + F_2^3(\epsilon)\} e^{-\epsilon/kT} d\epsilon = 0, \text{ (all } T),$$

which are also equivalent to components of (15). Equations (15) are therefore the necessary and sufficient conditions for the preservation of the regular equilibrium distribution laws. It may no doubt still be true that the three F 's in (15) are severally zero for all ϵ , or in other words that equations of type (8) are true for each type of switch present. But such equations are not a logical consequence of our premises.

In the general case we may expect to obtain only $n-1$ relations between $\frac{1}{2}n(n-1)$ functions F .

Before leaving the consideration of this mechanism, let us remove the restriction that the atoms are fixed. This general case is of practical importance in all except electronic collisions, for it is only then that the random velocities of the atoms are in fact negligible. The relative orbit of the incident electron (or other particle) is determined by the relative velocity V , the usual distance p and the atomic orientation. It is obvious that the average chance of a successful collision of any type must be a function of V and p only. The total number of collisions for which V and p lie between $V, V+dV$ and $p, p+dp$ is given by the well-known formula *

$$4\pi xy \left\{ \frac{mM}{2\pi kT(M+m)} \right\}^{3/2} e^{-\frac{1}{2kT} \frac{MmV^2}{M+m}} V^3 dV \cdot 2\pi p dp. \quad (17)$$

But the energy of the motion of the system atom-electron relative to its centre of gravity is $\frac{1}{2}MmV^2/(M+m)$ before the encounter has effectively begun, and if the laws of conservation of linear momentum are to be preserved in these processes, it is this energy of the relative motion only, not *e.g.* $\frac{1}{2}mV^2$, which is available for transformation into atomic energy in a collision of the first kind. Such inelastic collisions will therefore now only begin to occur when

$$\frac{1}{2} \frac{Mm}{M+m} V^2 > \epsilon_{12}.$$

Under these conditions (but under no others) the two processes can fit together to preserve the ordinary equilibrium. If ϵ now denotes $\frac{1}{2}MmV^2/(M+m)$, the expression (17) reduces to (2) and the necessary and sufficient condition for preservation of the equilibrium with an atom of two levels is given by (8) as before.

§ 3. The unit mechanism based on the process of ionization by collision.

We shall in this section consider only fixed atoms, equivalent to atoms of infinite mass. We know that a process can occur in which an e -electron (or other particle) can knock another electron out of an atom, provided that $\epsilon > \epsilon_0$, where ϵ_0 is the energy necessary to remove this electron. This process of ionization by collision can certainly occur when ϵ only just exceeds ϵ_0 , so that there is no reason to suppose that radiation need play any essential part. It seems very probable, from a study of β -ray tracks, that we

* Jeans, 'Dynamical Theory of Gases,' ed. 3. formula (701).

may suppose that the remaining part of the energy $\epsilon - \epsilon_0$ can be distributed in any manner between the two electrons after the collision, and that, whatever ϵ , we may suppose that a process of exchange of this type can occur without the emission or absorption of radiation. Coupled with this process of ionization there must be some process of capture, which for all values of the temperature and concentrations will preserve the laws of dissociative equilibrium. Together these processes of ionization and capture will form a unit mechanism. The process of ionization which we contemplate here is radiationless. So also must therefore be the process of capture. It is not difficult to convince oneself that the only possible (suitable) process of capture is a collision of three bodies, two electrons and one ionized atom, in which the two electrons so interact that one of them is bound by the atom and the other is thrown off with the kinetic energy of both before collision and the ionization energy ϵ_0 thrown in. If the superfluous energy may not be radiated, it can only be carried off by at least one other material body. That such a process, the strict reverse of ionization by collision, occurs can hardly be a novel idea. Its possible great importance does not seem to have been recognized.

The number of collisions with ϵ -electrons and line of impact between p and $p+dp$ is given by (2). Let us suppose here that the only possible result is ionization (provided $\epsilon > \epsilon_0$), after which there will be two free electrons, a new η -electron, and the old one, now an $(\epsilon - \epsilon_0 - \eta)$ -electron. It is necessary that $\epsilon - \epsilon_0 - \eta > 0$. The probability of such a result must have a definite value depending on p , η , and ϵ . We define $\Sigma_1^2(p, \eta, \epsilon)d\eta$ to be the probability of ionization with the production of a new η -electron with energy between η and $\eta+d\eta$. To find the total production of η -electrons in this way we have to integrate with respect to p . Writing

$$2\pi \int_0^\infty p \Sigma_1^2(p, \eta, \epsilon) dp = S_1^2(\eta, \epsilon), \quad \dots \quad (18)$$

the total is

$$x_1 \left(\frac{2\epsilon}{m} \right)^{1/2} \mu(\epsilon) d\epsilon \cdot S_1^2(\eta, \epsilon) d\eta. \quad \dots \quad (19)$$

The total rate of production of ions in this way must be obtained by integrating η from 0 to $\epsilon - \epsilon_0$ and then ϵ from ϵ_0 to ∞ . There is a simple physical meaning for

$$\int_0^{\epsilon - \epsilon_0} S_1^2(\eta, \epsilon) d\eta.$$

It is the mean effective collision area for ionization by ϵ -electrons.

The reverse three-body process can be similarly formulated. Consider first of all an ionized atom in process of being hit by a ζ -electron on a line of impact between p_1 and $p_1 + dp_1$. There are

$$x_1 \cdot 2\pi p_1 dp_1 \cdot \left(\frac{2\zeta}{m}\right)^{1/2} \mu(\zeta) d\zeta$$

of these occurrences per unit volume per second. The other electron is to enter into collision on a path on which (if undisturbed) it would reach its apse at a time between τ and $\tau + d\tau$ seconds after the first electron reached its apse. With every collision with a ζ -electron there is therefore associated a volume

$$\left(\frac{2\xi}{m}\right)^{1/2} d\tau \cdot 2\pi p_2 dp_2,$$

in which a ξ -electron may lie whose passage through its apse on a p_2 -line of impact would occur in the specified interval. Our expectation of ξ -electrons in this volume is

$$\left(\frac{2\xi}{m}\right)^{1/2} d\tau \cdot 2\pi p_2 dp_2 \cdot \mu(\xi) d\xi.$$

The number of three-body collisions, in which ζ -electrons and ξ -electrons with p_1 - and p_2 -lines of impact and time difference τ are concerned, is therefore

$$x_1 \left(\frac{2\zeta}{m}\right)^{1/2} \mu(\zeta) d\zeta \cdot \left(\frac{2\xi}{m}\right)^{1/2} \mu(\xi) d\xi \cdot 2\pi p_1 dp_1 2\pi p_2 dp_2 d\tau. \quad (20)$$

This number has been so specified that it disregards the relative directions of the lines of impact of the electrons and the atomic orientation. Averaged over all such directions and orientations there will be a certain definite probability $\Sigma_1^1(p_1, p_2, \tau, \zeta, \xi)$ that any one of these collisions leads to a successful interaction by which the ζ -electron is bound and the ξ -electron thrown off as a $(\xi + \zeta + e_0)$ -electron. Writing

$$4\pi^2 \int_0^\infty p_1 dp_1 \int_0^\infty p_2 dp_2 \int_{-\infty}^{+\infty} \Sigma_2^1(p_1, p_2, \tau, \zeta, \xi) d\tau = S_2^1(\zeta, \xi), \quad (21)$$

which will then be a purely atomic function of dimensions $[L]^4 [T]$, we can express the number of successful triple collisions in which a ζ -electron is bound by the interaction of a ξ -electron in the form

$$x_1 \left(\frac{2\zeta}{m}\right)^{1/2} \mu(\zeta) d\zeta \cdot \left(\frac{2\xi}{m}\right)^{1/2} \mu(\xi) d\xi \cdot S_2^1(\zeta, \xi). \quad (22)$$

These collisions each create a neutral atom and a $(\xi + \zeta + \epsilon_0)$ -electron at the expense of an ion, a ξ -electron and a ζ -electron.

The appropriate law of dissociative equilibrium* is believed to be

$$\frac{x_2 y}{x_1} = e^{-\epsilon_0/kT} \frac{(2\pi m kT)^{3/2} \sigma}{q h^3} \dots \dots \dots (23)$$

where h is Planck's constant, σ the so-called symmetry number of the neutral atom, and q the weight of its normal state relative to the ion. If the suggested processes form a unit mechanism they must preserve (23), subject only to certain purely atomic functional relations between S_1^2 and S_2^1 . Alternatively (19) and (22) must lead to an equation equivalent to (23) if we prefer to formulate the argument this way round. The necessary functional relations are very simple.

Consider first the preservation of the balance of the electronic distribution laws for η -electrons, $\eta < \epsilon_0$. By the process of ionization new electrons are produced by ϵ -electrons at rate (19) and the old ϵ -electrons are converted to η -electrons when the new ones are $(\epsilon - \epsilon_0 - \eta)$ -electrons. The combined rate of production of η -electrons in ionization by ϵ -electrons is thus

$$x_1 \left(\frac{2\epsilon}{m}\right)^{1/2} \mu(\epsilon) d\epsilon \{S_1^2(\eta, \epsilon) + S_1^2(\epsilon - \epsilon_0 - \eta, \epsilon)\} d\eta,$$

when $\epsilon < \epsilon_0 + \eta$, and is otherwise zero. The total rate of production of η -electrons is therefore

$$x_1 d\eta \int_{\epsilon_0 + \eta}^{\infty} \left(\frac{2\epsilon}{m}\right)^{1/2} \{S_1^2(\eta, \epsilon) + S_1^2(\epsilon - \epsilon_0 - \eta, \epsilon)\} \mu(\epsilon) d\epsilon, \quad (24)$$

per unit volume per second by the ionization process. This holds for all η , but when $\eta < \epsilon_0$ there is no destruction of η -electrons by this process.

Taking now the capture process, we see at once that it produces no η -electrons ($\eta < \epsilon_0$) for the resulting free electron has always an energy greater than ϵ_0 . It destroys each time both a ζ - and a ξ -electron. The total number of η -electrons destroyed by binding (ξ -type) is therefore

$$x_2 \left(\frac{2\eta}{m}\right)^{1/2} \mu(\eta) d\eta \int_0^{\infty} \left(\frac{2\xi}{m}\right)^{1/2} S_2^1(\eta, \xi) \mu(\xi) d\xi.$$

* See, for instance, Fowler and Milne, *Monthly Notices R. A. S.*, lxxxiii. p. 407 (1923). The only doubtful points in (23) are connected with the values of σ and q . But their precise values are irrelevant here. We are assuming in this discussion that the neutral atom has only one possible stationary state.

The corresponding number destroyed by conversion into fast electrons (ξ -type) is

$$x_2 \left(\frac{2\eta}{m} \right)^{1/2} \mu(\eta) d\eta \int_0^\infty \left(\frac{2\xi}{m} \right)^{1/2} S_2^1(\xi, \eta) \mu(\xi) d\xi.$$

The grand total of destructions of η -electrons per unit volume per second is therefore

$$x_2 \left(\frac{2\eta}{m} \right)^{1/2} \mu(\eta) d\eta \int_0^\infty \left(\frac{2\alpha}{m} \right)^{1/2} \{S_2^1(\eta, \alpha) + S_2^1(\alpha, \eta)\} \mu(\alpha) d\alpha, \quad (25)$$

for all values of η . For preservation of the distribution laws we must have

$$\begin{aligned} x_2 \left(\frac{2\eta}{m} \right)^{1/2} \mu(\eta) d\eta \int_0^\infty \left(\frac{2\alpha}{m} \right)^{1/2} \{S_2^1(\eta, \alpha) + S_2^1(\alpha, \eta)\} \mu(\alpha) d\alpha \\ = x_1 d\eta \int_{\epsilon_0 + \eta}^\infty \left(\frac{2\epsilon}{m} \right)^{1/2} \{S_1^2(\eta, \epsilon) + S_1^1(\epsilon - \epsilon_0 - \eta, \epsilon)\} \mu(\epsilon) d\epsilon, \\ (\eta < \epsilon_0). \quad \dots \quad (26) \end{aligned}$$

When we use equations (1) and (23), equation (26) reduces to

$$\begin{aligned} \int_0^\infty e^{-\alpha/kT} (\epsilon_0 + \eta + \alpha) \{S_1^2(\eta, \epsilon_0 + \eta + \alpha) + S_1^1(\alpha, \epsilon_0 + \eta + \alpha)\} d\alpha \\ = \frac{8\pi m \sigma}{q h^3} \int_0^\infty e^{-\alpha/kT} \alpha \eta \{S_2^1(\eta, \alpha) + S_2^1(\alpha, \eta)\} d\alpha, \quad (\eta < \epsilon_0). \quad (27) \end{aligned}$$

If equation (27) is to hold for all T , it follows at once by the Lemma that we must have

$$\begin{aligned} (\epsilon_0 + \eta + \alpha) \{S_1^2(\eta, \epsilon_0 + \eta + \alpha) + S_1^1(\alpha, \epsilon_0 + \eta + \alpha)\} \\ = \frac{8\pi m \sigma}{q h^3} \alpha \eta \{S_2^1(\eta, \alpha) + S_2^1(\alpha, \eta)\}, \quad \dots \quad (A) \end{aligned}$$

for all α and all $\eta < \epsilon_0$. We may observe that if we do not assume (23), we can deduce its form as a function of T , without of course an explicit value for the constant, from the facts that (26) must be true for all T , and that the atomic coefficients S cannot depend on the temperature and the pressure.

It is necessary in addition that the rates of production and destruction of atomic ions should balance. The condition is easily obtained. It is

$$\begin{aligned} x_1 \int_{\epsilon_0}^\infty \left(\frac{2\epsilon}{m} \right)^{1/2} \mu(\epsilon) d\epsilon \int_0^{\epsilon - \epsilon_0} S_1^2(\eta, \epsilon) d\eta \\ = x_2 \int_0^\infty \int_0^\infty \left(\frac{2\xi}{m} \right)^{1/2} \left(\frac{2\zeta}{m} \right)^{1/2} \mu(\zeta) \mu(\xi) S_2^1(\zeta, \xi) d\zeta d\xi. \quad (27') \end{aligned}$$

Making the same substitutions, this reduces to

$$\begin{aligned} & \int_0^\infty (\epsilon_0 + \alpha) e^{-\alpha/kT} d\alpha \int_0^\alpha S_1^2(\eta, \epsilon_0 + \alpha) d\eta \\ &= \frac{8\pi m\sigma}{qh^3} \int_0^\infty \int_0^\infty \xi \xi e^{-(\xi+\xi)/kT} S_2^1(\xi, \xi) d\xi d\xi \\ &= \frac{8\pi m\sigma}{qh^3} \int_0^\infty e^{-\alpha/kT} d\alpha \int_0^\alpha \eta(\alpha - \eta) S_2^1(\eta, \alpha - \eta) d\eta, \quad (28) \end{aligned}$$

for all values of T. Therefore by the Lemma

$$\begin{aligned} & (\epsilon_0 + \alpha) \int_0^\alpha S_1^2(\eta, \epsilon_0 + \alpha) d\eta \\ &= \frac{8\pi m\sigma}{qh^3} \int_0^\alpha \eta(\alpha - \eta) S_2^1(\eta, \alpha - \eta) d\eta, \quad (\text{all } \alpha). \quad (B) \end{aligned}$$

It remains to consider the electron balance for $\eta > \epsilon_0$, which in virtue of (B) we shall find to be conserved if (A) holds for all η as well as for all α . Expressions (24) and (25) still give the production by ionization and the destruction by capture. There is now in addition a destruction of η -electrons by ionization at a rate

$$x_1 \left(\frac{2\eta}{m} \right)^{1/2} \mu(\eta), d\eta \int_0^{\eta - \epsilon_0} S_1^2(\alpha, \eta) d\alpha, \quad . \quad . \quad (29)$$

equal of course to the rate of production of ions by η -electrons. There is also a production by capture. The first argument of $S_2^1(\xi, \xi)$ refers to the electron that is bound. The energy of the electron left free, on binding a ξ -electron in interplay with a ξ -electron, is $\xi + \xi + \epsilon_0$. If, therefore, $\xi + \xi + \epsilon_0 = \eta$, we have to sum up all triple encounters of the type

$$\xi, \eta - \epsilon_0 - \xi, \quad (0 < \xi < \eta - \epsilon_0),$$

and shall so find that η -electrons are produced at a rate

$$\begin{aligned} & x_2 d\eta \int_0^{\eta - \epsilon_0} \left(\frac{2\xi}{m} \right)^{1/2} \left\{ \frac{2(\eta - \epsilon_0 - \xi)}{m} \right\}^{1/2} \mu(\xi) \mu(\eta - \epsilon_0 - \xi) \\ & \quad S_2^1(\xi, \eta - \epsilon_0 - \xi) d\xi. \quad (30) \end{aligned}$$

The electron equation now contains four terms and equates (24) and (30) to (25) and (29). But on account of (B) the extra terms (29) and (30) balance by themselves. For they will so balance if

$$\frac{8\pi m\sigma}{qh^3} \int_0^{\eta - \epsilon_0} \xi(\eta - \epsilon_0 - \xi) S_2^1(\xi, \eta - \epsilon_0 - \xi) d\xi = \eta \int_0^{\eta - \epsilon_0} S_1^2(\alpha, \eta) d\alpha,$$

which is equivalent to (B). The validity of (A) must therefore be unlimited, and the necessary and sufficient conditions for the preservation of the laws of dissociative equilibrium are that (A) should hold for all α and η , and (B) for all α .

It will be noticed at once that (B) is obtained by equating the first terms only from the two sides of (A), and integrating in a suitable manner. Though it is not a logical consequence of (A) and (B) it seems not at all unlikely that the single relation that really holds is

$$(\epsilon_0 + \eta + \alpha) S_1^2(\eta, \epsilon_0 + \eta + \alpha) = \frac{8\pi m \sigma}{q h^2} \alpha \eta S_2^1(\eta, \alpha). \text{ (all } \alpha, \eta). \text{ (C)}$$

Equation (C) implies both (A) and (B). It is obviously (C) which would have to hold, if we had to distinguish the two electrons in these processes and no longer regard as interchangeable the bombarding electron (or electron thrown off at high speed) and the electron knocked out of the atom (or bound by the atom). In the case discussed here such a distinction is meaningless, but the arguments apply equally to the case of radiationless dissociations and recombinations in which the three bodies concerned are all different * [for example, perhaps molecular dissociations by electronic or atomic impacts or ionization by bombardments by protons or α -particles]. In such cases the necessary and sufficient relations must be of type (C), and it seems reasonable to suppose that it is equation (C), and not the slightly less restrictive (A) and (B), which holds also in this case.

There is an obvious field for the extension of these arguments to atoms with more than one ionization potential, corresponding to the removal of different electrons, or of the same electron from different orbits. There is also the restriction to fixed atoms to be removed. These are just the extensions which we have made in Klein and Rosseland's work in the beginning of this paper, and they are obviously of some importance. Their consideration cannot be undertaken here.

We note in conclusion that (C) throws perhaps a little light on the meaning of σ and q . The value of σ appears from other chains of reasoning to be equal to the number of electrons in equivalent (most tightly bound) orbits. We should therefore expect S_1^2 to be proportional to σ , as each of these electrons must contribute equally to the mean effective target for the removal of any one of them. The value of q , the weight of the normal orbit of the returning electron, appears to be equal to the number of equivalent

* Provided of course that we may treat the main atoms as fixed.

ways in which the electron can be bound. We should expect S_2^1 to be proportional to q , for each of these ways might be expected to contribute equally to the chances of binding.

§ 4. *The evidence of β -ray results for the form of $S_1^2(\eta, \epsilon)$ and $S_2^1(\eta, \epsilon)$.*

It is possible to estimate the mean collision area for ionization with the ejection of an η -electron by a study of the theory and experiments on the passage of β -rays through gases. The classical theory of this phenomenon developed by J. J. Thomson* and Bohr† seems to apply with very considerable accuracy. It leads to the V^4 -law for ranges, which is fairly closely obeyed, though the value of the numerical coefficient in the stopping power to which it leads is somewhat too small‡ (by a factor perhaps of 2 or 3). Moreover, a further slight extension of the theory by the present writer§, in which we require to know only the relative frequencies with which η - and η' -electrons are ejected, leads to the result that the average expenditure of energy by the β -ray per pair of ions made should be four-thirds of the ionization potential. This result seems to be confirmed by the recent experiments of C. T. R. Wilson||, in which he finds the value 26 volts per ion-pair in air. Since air is mainly N_2 with a first ionization potential of 17 volts, we should expect from the theory at least 23–24 volts expenditure per ion-pair.

These experimental confirmations refer mainly to high velocities of the electron, but it is with lower velocities, especially those just greater than ϵ , with which we are mainly concerned. More information in this region is greatly to be desired. But even here the β -ray theory gives results which are at least of the expected order. It is shown in the next paragraph that the effective area given for ionization is

$$\frac{\pi \sigma e^4}{\epsilon} \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon} \right)$$

where e is the electronic charge. This has a maximum when $\epsilon = 2\epsilon_0$ whose value is $\pi \sigma e^4 / 4\epsilon_0^2$. For an atom for which

$$\epsilon_0 = 10 \text{ volts} = 10 \times 1.591 \times 10^{-12} \text{ erg,}$$

* J. J. Thomson, Phil. Mag. xxiii. p. 449 (1912).

† Bohr, *ibid.* xxiv. p. 10 (1913); xxx. p. 581 (1915).

‡ C. T. R. Wilson, Proc. Roy. Soc. A. civ. pp. 1, 192 (1923), in particular pp. 196, 199.

§ Fowler, Proc. Camb. Phil. Soc. xxi. p. 521 (1923).

|| Wilson, *loc. cit.* p. 200.

this area works out at $1.56\sigma \times 10^{-16}$ cm.², so that if allowance is made for a factor of 2 or 3, the theory indicates that the maximum effective area is the whole area of the atom; this result would seem to be agreeable to the work of Franck and others on ionization potentials. In a first rough survey it therefore seems legitimate to take the classical theory as it stands, for both high and low velocities, as giving correctly the relative frequencies of ejection of η - and η' -electrons, and a numerical coefficient for the absolute frequency at least of the right order.

If then for the moment p denotes the distance of the line of impact of the ϵ -electron from the electron which it is to knock out of the atom, there is a precise relation between this p and η , namely *,

$$p^2 = \frac{e^4}{\epsilon^2} \left(\frac{\epsilon}{\eta + \epsilon_0} - 1 \right) \dots \dots \dots (31)$$

or

$$2\pi p dp = \frac{\pi e^4}{\epsilon} \frac{d\eta}{(\eta + \epsilon_0)^2} \dots \dots \dots (32)$$

This is the mean effective target of our theory for each equivalent electron. In our notation $\Sigma_1^2(p, \eta, \epsilon) d\eta = 1$ for this region, and is otherwise zero. Thus

$$S_1^2(\eta, \epsilon) = \frac{A\sigma}{\epsilon} \frac{1}{(\eta + \epsilon_0)^2}, (A = \pi e^4), \dots \dots \dots (33)$$

with some doubts as to the numerical factor in A . For the process of capture

$$\frac{8\pi m \sigma}{\eta h^3} \alpha \eta S_2^1(\eta, \alpha) = (\epsilon_0 + \eta + \alpha) S_1^2(\eta, \epsilon_0 + \eta + \alpha) = \frac{A\sigma}{(\eta + \epsilon_0)^2}, (34)$$

$$S_2^1(\eta, \alpha) = \frac{q h^3}{8\pi m \alpha \eta} \frac{A}{(\eta + \epsilon_0)^2} \dots \dots \dots (35)$$

This makes the mean effective collision "time-(area)²" for capture $\rightarrow \infty$ as $\alpha \rightarrow 0$ or as $\eta \rightarrow 0$. This is perhaps unexpected, but is not in any way physically impossible.

§ 5. The comparative numerical frequency of radiative (photo-electric) and radiationless (collision) ionizations and captures in a gaseous assembly.

The calculations that follow do not essentially depend on the foregoing discussion which has established the relation between S_1^2 and S_2^1 . To estimate the relative importance of the two processes it is really only necessary to compare

* Fowler, *loc. cit.*

the numbers of ionizations by collision and by the photo-electric effect, and S_2^1 need not be referred to. But it seems proper to give the calculations here, since the preceding considerations seem to give them point. A grasp of the consequences of the idea of the unit mechanism makes it easier to regard the calculation as determining the relative importance of two unit mechanisms as wholes, and it is in this that its main value lies.

Using (1) and (33) we find for the rate of ionization per cubic centimetre per second

$$\begin{aligned} n_{\text{coll}} &= \frac{8\pi\sigma x_1 y}{(2\pi kT)^{3/2} m^{1/2}} \int_{\epsilon_0}^{\infty} \epsilon e^{-\epsilon/kT} d\epsilon \int_0^{\epsilon-\epsilon_0} A \frac{d\eta}{\epsilon(\eta+\epsilon_0)^2}, \\ &= \frac{8\pi\sigma A x_1 y e^{-\epsilon_0/kT}}{(2\pi kT)^{3/2} m^{1/2}} \int_0^{\infty} \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_0 + \alpha} \right) e^{-\alpha/kT} d\alpha. \quad \dots (36) \end{aligned}$$

The integral contains the logarithmic integral and cannot be evaluated in finite terms. When kT/ϵ_0 is fairly small, it is represented closely by the asymptotic expansion

$$\int_0^{\infty} \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_0 + \alpha} \right) e^{-\alpha/kT} d\alpha \sim \left(\frac{kT}{\epsilon_0} \right)^2 - 2! \left(\frac{kT}{\epsilon_0} \right)^3 + 3! \left(\frac{kT}{\epsilon_0} \right)^4 - \dots, \quad \dots (37)$$

with an error always less than the last term retained. The rate of ionization by collision when kT/ϵ_0 is small enough for the first term of (37) to be a fair representation of the integral is therefore

$$n_{\text{coll}} \sim \frac{8\pi\sigma A x_1 y e^{-\epsilon_0/kT} (kT)^{1/2}}{(2\pi)^{3/2} m^{1/2} \epsilon_0^2}, \quad \left(\frac{kT}{\epsilon_0} \text{ small} \right), \quad \dots (38)$$

Now Milne* has shown that the number of photoelectric ionizations per cubic centimetre per second in a gaseous assembly in thermodynamic equilibrium is

$$x_1 \int_{\nu_0}^{\infty} \psi(\nu) I(\nu) d\nu \quad \dots (39)$$

where ν_0 is the series limit for the state of the atom concerned, i. e. $h\nu_0 = \epsilon_0$, and

$$\psi(\nu) = \frac{4\pi^2 m^2 \sigma}{c q} \mu \left(\frac{c}{h\nu} \right)^3, \quad \dots (40)$$

$$I(\nu) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1} \quad \dots (\text{Planck's Law}) \quad (41)$$

* *Loc. cit.*

It appears theoretically that μ is a certain function of ν , or better of v the velocity of the corresponding photoelectron. It appears empirically that μ is probably a constant at least in the most important region. The stellar evidence from Eddington's theory of giant stars, together with certain evidence from optical absorption coefficients for resonance radiation, agree in indicating that $\mu=10^{-4}Z$, where Z is the atomic number. Taking $Z=1$, hydrogen, for illustration, the number of photoelectric ionizations per cubic centimetre per second then reduces to

$$n_{\text{rad}} = \frac{8\pi^2 m^2 \sigma_{\text{r}_1}}{qh^3} 10^{-4} kT \int_{\epsilon_0/kT}^{\infty} \frac{dx}{e^x - 1} \quad \dots (42)$$

When kT/ϵ_0 is fairly small this is approximately

$$n_{\text{rad}} \propto \frac{8\pi^2 m^2 \sigma_{\text{r}_1}}{qh^3} 10^{-4} kT e^{-\epsilon_0/kT}, \quad \left(\frac{kT}{\epsilon_0} \text{ small} \right) \quad \dots (43)$$

The ratio $n_{\text{coll}}/n_{\text{rad}}$ is of great interest. We find using (38) and (43)

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = \frac{10^4 A q h^3}{2^{3/2} (\pi m)^{5/2}} \cdot \frac{\eta}{\epsilon_0^2 (kT)^{1/2}} \quad \dots (44)$$

Strictly speaking (44) is valid only for kT/ϵ_0 small, but it will give the correct order for this ratio in a wider range of cases.

If we take the classical value of A , and express all energies in volts we find *

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = 1.15 \times 10^{-16} \frac{\eta \eta}{\epsilon_0^2 (kT)^{1/2}}, \quad (\text{energies in volts}). \quad (45)$$

If we take the case of a typical stellar reversing layer at $10,000^\circ$, $kT=0.86$, an electron pressure of 10^{-4} atmosphere, $\eta=7.86 \times 10^{13}$, and say hydrogen atoms in the Balmer state, $q=6$, $\epsilon_0=3.39$ volts, we find

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = 5.1 \times 10^{-3}.$$

Thus in any problem of a stellar reversing layer the effect of the captures and ionizations by collision with electrons is

* I have preferred at this stage to compare the relative frequencies of radiative and collision processes on the basis of Milne's semi-empirical formulation of the frequencies of the radiative processes rather than on the basis of Kramer's wholly theoretical discussion, which needs somewhat careful and critical interpretation for application to the cases in point here.

practically nil. The control they will exercise when thermodynamic equilibrium is disturbed by the flow of radiation of a different temperature is negligible*.

The case discussed by Eddington† of the interior of a star turns out to be slightly different. His typical conditions involve an electron density $\gamma = 1.356 \times 10^{22}$, and a temperature °C. of 5.64×10^6 . The average ionization must have proceeded to a stage such that for the orbits in which we are interested the ionization potentials will lie in the range 600–1000 volts. In such a case we should find

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = 1.2 - 0.42,$$

or 1/6th of these values if we should take $q=1$. The two types of capture and ionization are now of the same order of frequency, with the radiative type even now somewhat more frequent.

This calculation does not agree with some tentative evaluations of this ratio by Lindemann‡ in a criticism of Eddington's theory of capture. Lindemann suggests a ratio 10,000 instead of 1, but it is apparent on reading his note that he has ignored the change in target area due to the increase in binding of the relevant electrons, which is allowed for here by the factor ϵ_0^2 in the denominator. This is a factor of the order 10,000 precisely, and its insertion brings his estimate into full agreement with the estimate made here. It should be remembered, however, that whatever the value of the ratio, Eddington's *general* argument that radiative captures will exactly balance photoelectric ionizations is almost certainly sound. Ionizations by collision will balance captures by collision, and Lindemann's criticism so far as it affects the *general* argument appears to rest on a misconception.

The examples above show collision captures to be of somewhat slight importance in the cases specified. This, however, will by no means always be the case. As we descend towards the photosphere from the reversing layer the pressure rises very rapidly indeed compared with the temperature. We should reach a pressure of, for example, 1 or 10 atmospheres with a hardly significant rise in temperature. In these conditions for hydrogen in the Balmer

* It is not difficult to verify in addition that the effect of collisions by the hydrogen or other nuclei will on the same basis be in general negligible compared with that of the electronic collisions.

† Eddington, Monthly Notices R. A. S. lxxxiii. p. 32 (1922).

‡ Lindemann, Monthly Notices R. A. S. lxxxiii. p. 332 (1923).

state we obtain from (45), roughly,

$$\frac{n_{\text{coll}}}{n_{\text{rad}}} = 50-500.$$

These rapid changes in the relative importance of radiative and radiationless processes are probably significant, as we have suggested in the introduction.

§ 6. *Summary.*—Klein and Rosseland's theory of collisions of the first and second kind is discussed and further amplified. It is shown what type of relations can be strictly deduced in the case of atoms with more than two stationary states: also how to formulate the theory when the atoms are no longer assumed to be of infinite mass.

The same ideas are extended to the mechanism of ionization by collision. The reverse process is a three-body collision and the necessary frequency relation is determined.

The theory and experimental results of ionization by β -particles is applied to deduce the form of the frequency function for one of these processes (ionization) and the frequency function for the other is deduced.

The relative importance of collision processes and radiative processes is formulated and discussed in a number of cases, for gaseous assemblies. It is shown that either type may be dominant.

XXIV. *The Capture and Loss of Electrons by α Particles.* By Professor Sir E. RUTHERFORD, F.R.S., Cavendish Professor of Experimental Physics, University of Cambridge*.

IN a recent paper, G. H. Henderson† has given an account of some very interesting experiments on the capture and loss of electrons by α particles. The photographic effect of a pencil of α rays was examined in a magnetic field by the photographic method, using Schumann plates. In a high vacuum, in addition to the main deflected band due to doubly-charged α particles, there appeared a "midway" band which suffered only half the deflexion of the main band. This band was ascribed to α particles which had captured an electron and which were thus bent by the magnetic field to only half the extent of the main band. As the velocity of the α particles was reduced by increasing thickness of mica over the source, the midway band became

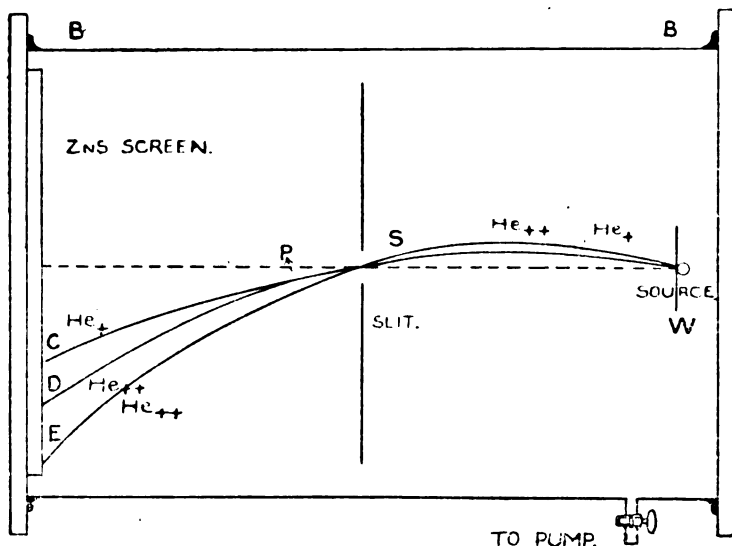
* Communicated by the Author.

† Proc. Roy. Soc. A, cii. p. 496 (1922).

more and more prominent, and ultimately an undeflected band due to neutral helium particles was observed. For the success of these experiments it was essential that the apparatus should be exhausted to the stage of a cathode-ray vacuum. The presence of a small trace of residual gas caused the disappearance of the neutral and midway band. The failure of previous investigators to note the effects observed by Henderson is to be ascribed to the presence of residual gas in the path of the rays in their experiments.

While of course it had always been supposed that the α particle captured electrons near the end of its path, it had not been expected that the α particle could capture an electron in the early part of its range. It was of importance

Fig. 1.



to verify the conclusion of Henderson by the scintillation method where the energy of the particles can be estimated by the brightness of the scintillations and their number determined by direct counting. At the same time it was of much interest to test whether methods could be devised for determining the frequency of capture and loss of electrons by the α particles and its variation with the velocity of the α particle.

The general method * employed is shown in fig. 1. The

* A preliminary account of these experiments was published in the Proc. Camb. Phil. Soc. xxi. p. 504 (1923).

radioactive source consisted of a fine platinum wire W (·3 mm. in diameter), coated with radium B and C, and placed in an exhausted box B. The rays passed through a fine slit S and fell on a zinc-sulphide screen placed inside the box. The scintillations were viewed through a glass plate by a microscope in the usual way. The microscope was arranged to have a vertical motion so that any part of the screen could be brought into view. The slit was equidistant, viz. 8 cm., from the source and screen, and a magnetic field of about 6000 gauss was ordinarily applied perpendicular to the path of the rays. In these experiments it is very important to avoid radioactive contamination of the box and screen. This is very difficult to effect when an uncovered source is used. In the low vacuum required, traces of emanation are usually released from the source, and contaminate the whole box. In addition, if the source is placed in the box soon after removal from the emanation, the recoil of radium B causes a distribution of radioactive matter. Even when the source is not introduced into the box until radium A has practically disappeared, there is still the possibility of contamination due to the β -ray recoil of radium C from radium B. For these reasons, it was essential that the source should be completely covered in. The active wire was placed in a small chamber, covered with the requisite thickness of mica. This chamber could be exhausted during an experiment separately from the main box. The box containing the source and the charcoal tube for exhaustion was fixed rigidly to an ebonite ground-joint, which could be rapidly placed in position in the main box. The latter was initially exhausted by a Gaede pump and then by a Langmuir diffusion pump. The residual pressure of the gas in the box was measured by a Macleod gauge, and two liquid-air traps were in the circuit to prevent mercury vapour from the pump or gauge diffusing into the deflecting box. The field of view of the microscope (1·2 mm. wide) was more than sufficient to take in the whole width of the main band of homogeneous rays.

The distribution of the particles in the deflected beam, found by the scintillation method, is shown in figs. 2, 3, and 4 corresponding to different thicknesses of mica over the source. The emergent range of the α particles was about 3·6 cm. in fig. 2, 1·2 cm. in fig. 3, and 0·46 cm. in fig. 4. The abscissæ represent the actual deflexion of the particles in millimetres in each experiment, but the deflexions are not directly comparable, as the electromagnet was excited by different currents in each case.

In fig. 2 the midway band is deflected to exactly half the extent of the main band, but the number of particles in the

Fig. 2.

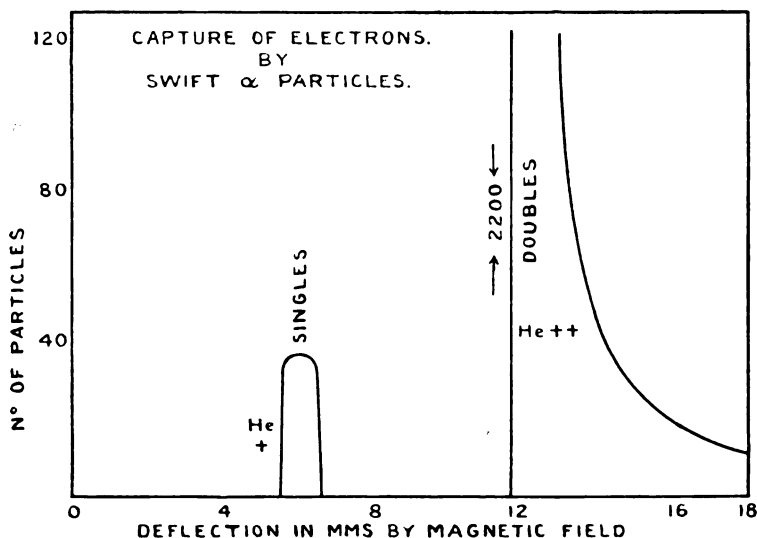
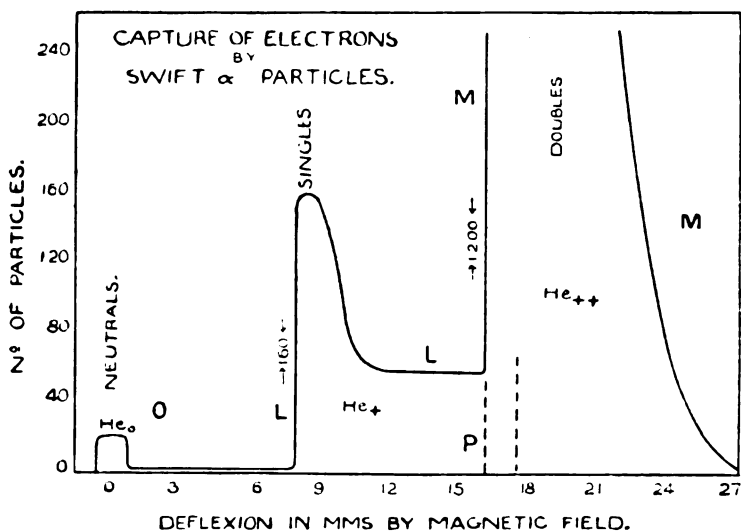


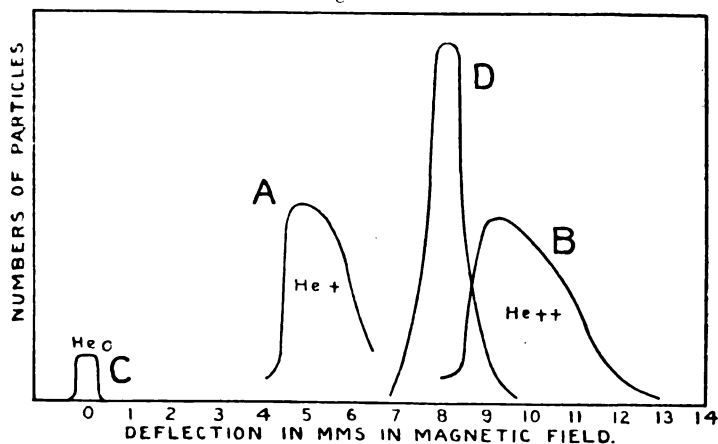
Fig. 3.



band is only $1/67$ of that in the main band. With lowering of the range of the emergent α particles, the curves change rapidly in shape. In fig. 3 the width of the deflected main

band MM is much wider than with zero field, showing that the α rays after traversing the mica vary markedly in velocity. The midway band LL begins sharply at the midway point between O and P, but extends with decreasing brightness of scintillations to the main band, where it can no longer be followed. A group of undeflected particles appears at O, while between O and L a small number of weak scintillations was observed. The origin of the latter, which are few in number compared with the neutral band, has been difficult to fix with certainty. They are probably in part due to α particles scattered at the edges of the slits and the sides of the box, and partly due to recoil atoms set in motion by collision with the α particles in their passage through the mica. In fig. 4, for still lower velocities it is

Fig. 4.



seen that the midway band A contains more than half the particles of the main band B, while the undeflected band C becomes relatively more prominent than in fig. 3. There is no longer a sharp inner edge in the two bands, but the maximum number of particles occurs at a considerably lower velocity than the beginning of the bands. The significance of curve D will be discussed later in the paper. It will be clear from these illustrations how rapidly the relative number of particles in the two bands and the distribution of the particles with velocity vary with the emergent range of the particles, *i.e.* with their average velocity.

It will be noted that the width of the band due to the doubly-charged α particles in figs. 3 and 4 is much greater

than the width of the same beam when undeflected by the magnetic field. This shows that the rays issuing from the mica are heterogeneous, consisting of particles with a considerable range of velocity. This heterogeneity of the beam is easily observed, even when the stopping-power of the mica is reduced to 2 cm. I hope in a later communication to discuss this question in more detail when more systematic measurements have been made. In addition to this heterogeneity of the beam due to the passage of the α particles through the mica, the active wire itself is responsible for a similar effect, but on a smaller scale. Some of the α particles from the wire source escape from the back of the wire, and thus are reduced in velocity by their passage through the metal. The relative number of particles escaping in this way which have all velocities from the maximum to zero depends on the diameter of the wire, but under the conditions of the experiment only amounted to a few per cent. of the total number in the pencil. When a magnetic field is applied, these particles give, so to speak, a continuous magnetic spectrum of α rays extending from the edge of the main band in the direction of lower velocities. The heterogeneity in the beam due to the source does not seriously influence the deduction from the experiments discussed in this paper, but is a factor to be taken into account in special experiments where a homogeneous pencil of α rays may be required. This effect could in part be eliminated by the use of specially prepared sources where the activity is concentrated only on the front surface of the source, but such sources are difficult to prepare in sufficient intensity.

Incidentally the determination of the magnetic spectrum of the doubly-charged α particles gave a method of fixing the lowest velocity of the α particle for which a scintillation could be detected. It was found that the scintillations decreased steadily in intensity with increase of the magnetic deflexion. Particles of velocity $\cdot 25V_0$, where V_0 is the maximum velocity of the α particles from radium C, could be readily counted, while particles of velocity $\cdot 15V_0$ gave faint scintillations which could only be counted with difficulty.

The number of particles due to doubly-charged, singly-charged, and neutral helium atoms, as shown in fig. 3, varied in number over such a wide range that sources over a range of intensity of 100 times would be required to determine the number with certainty. To overcome this difficulty, an arrangement equivalent to the rotating wheel

with a slit was employed. Between the outside of the box and the microscope objective a brass plate with a slit of known width described a reciprocating motion between guides. The simple apparatus required was driven by a low-g geared motor, so that the slit passed by the objective about four times a second. Using one slit of width 7.5 mm., the reduction ratio for number of scintillations was .30, with a slit 2.5 mm. about .10. Usually only the slit of width 7.5 mm. was employed in counting, since the average intensity of the scintillations decreased the narrower the slit. This was due to the fact that it was impossible in the experiment to arrange that the brass plate moved close to the surface of the zinc sulphide. For this reason, some of the light due to a scintillation, which ordinarily entered the objective of wide aperture, was cut off by the plate. This reduction in brightness of the scintillation was so marked that the slits of width 1 mm. or 2.5 mm. could only be used with certainty to count scintillations when α particles of high velocity were used. Since the intensity of the α -ray source decayed to about .14 of its initial value in the course of two hours, it was generally possible with the aid of the movable slits to compare numbers of α particles in the ratio of 1 to 50 in the course of a complete experiment.

The determination of the curves such as are shown in figs. 3 and 4 involved a large amount of work in counting scintillations. The scintillations became weak in intensity for velocities below $.2V_0$, and accurate counting trying and difficult.

Electrostatic deflection of α particles.

While the results obtained by the scintillation method were in general agreement with those obtained by Henderson, using the photographic method, and could be readily interpreted on the view that the α particle captures electrons in its passage through matter, it was of importance to settle definitely whether the particles in the midway beam consisted of singly-charged helium atoms moving with the same velocity as the corresponding particles in the main beam.

For this purpose, the deflexion of the midway band was determined in an electrostatic as well as in a magnetic field. A sheet of mica of about 6 cm. stopping-power was placed over the source, and the distribution of the particles was about the same as that shown in fig. 3. The left edge of the midway band was fairly sharply defined, and corresponded to a velocity of $.47V_0$. Two parallel brass plates 7 cm. long,

4 mm. apart, were fixed between the source and slit shown in fig. 1, and parallel to the slit so that the deflected beams of rays did not impinge on the side of the plates. By means of an Evershed motor generator, a P.D. of 3000 volts was applied between the plates. The magnetic field was first adjusted to give a reasonable deflexion of the midway band. The electric field was then added in the highly exhausted box, and the shift of the edge of the midway band was noted on reversal of the electric field. Similar observations were made on the edge of the main band. The settings of the cross wire of the microscope on the edge of the bands could be made with precision. The change of deflexion of the main band by reversal of the field due to 3000 volts was 3.27 mm., and for the midway band 1.63 mm. or almost exactly half. The deflexion of the highest velocity particles in the midway band in a magnetic field, as we have seen, is exactly half of the corresponding particles in the main beam.

Suppose M, V, E be the mass-velocity and charge of the α particles in the main beam, and m, u, e the corresponding values for the particles in the midway beam.

From the observed magnetic deflexions,

$$MV/E = 2mu'/e.$$

From the observed electrostatic deflexions,

$$MV^2/E = 2mu^2/e.$$

It thus follows that

$$u = V$$

and

$$e/m = \frac{1}{2}E/M.$$

It is thus clear that the particles of the midway band have the same velocity as the corresponding particles in the main beam—a fact confirmed by the equal brightness of the scintillations,—but the value e/m is half of that for the ordinary α particle. It seems quite certain from these results that the particles in the midway band are singly-charged atoms of helium, *i. e.* helium nuclei which have captured one electron. It is thus natural to suppose that the undeflected particles are neutral helium atoms arising from the capture of two electrons by the α particles.

Mean free path for capture and loss.

It is to be supposed that the α particle occasionally captures an electron, and this electron may be subsequently lost by collision with the molecules. We shall see later that, for high-velocity particles, the average distance traversed by

the α particles in the material before capturing an electron or losing its captured electron is small compared with the range of the α particle in the material. We may suppose that for a definite velocity the He_{++} particle has a mean free path λ_1 cm. in the material before capturing an electron. No doubt some of the particles have much shorter and others much longer paths than the average before capture, the relative numbers being determined by the law of probability. Similarly, it may be supposed that the He_+ particle has a mean free path λ_2 cm. before losing its attendant electron by collision with the molecules.

It will be seen later that the interchanges of charge of the α particle occur more than a thousand times in its range. It is thus clear that a temporary equilibrium must exist between the numbers of N_1 of He_{++} particles and the number N_2 of He_+ particles for any given velocity, such that the number of captures is nearly equal to the number of losses in traversing a small thickness dx of the material. Consequently

$$N_1 dx / \lambda_1 = N_2 dx / \lambda_2,$$

or

$$N_2 / N_1 = \lambda_2 / \lambda_1.$$

It is clear that the ratio N_2/N_1 can be directly determined for any velocity by comparing the number of singly- and doubly-charged particles escaping from the mica in a vacuum over the same small range of velocities. The ratio λ_2/λ_1 is thus known.

This relation obviously applies not only to a definite beam of homogeneous rays, but to each constituent of a pencil of heterogeneous rays such as are shown in figs. 3 or 4. If the distribution curves are obtained accurately for He_{++} and He_+ , it is clear that the ratios λ_2/λ_1 can be obtained over a considerable range of velocity from a single experiment.

The mean free path λ_2 for loss of an electron from He_+ can be directly measured in the following way. Suppose the microscope is placed in such a position as to include the particles on the inside edge L of the midway band (fig. 3) and the number of scintillations counted in a high vacuum. When a gas at low pressure is introduced into the box, some of the He_+ particles lose an electron by a collision, and are deflected away from the field of view of the microscope. For example, the loss of an electron at P (fig. 1) will cause the particle to strike the screen at D instead of at C. It was found that the number of scintillations decreased nearly according to an exponential law with the pressure of the gas,

and ultimately became too small to count for a pressure of gas not sufficient to alter sensibly the velocity of the rays in traversing the gas. In these experiments, appropriate quantities of the dry, purified gases under examination were successively introduced by means of side tubes. It was found essential to have a liquid-air trap between the box and the Macleod gauge in order to prevent any mercury vapour entering the box. If the Langmuir pump were cut off from the highly exhausted box and the liquid air then removed from the trap between the box and the Macleod gauge, there was a rapid decrease in the intensity of the midway band as the pressure of mercury vapour in the box gradually rose. This experiment shows how effective is even a small pressure of mercury vapour in converting He_+ into He_{++} . For the higher velocities of the α particle the conversion of He_{++} into He_+ in the passage of the rays through the gas did not appreciably affect the result. With diminished velocity, this effect became noticeable. For example, using α particles of maximum velocity $\cdot 47V_0$ corresponding to fig. 3, the number did not fall to zero with increasing pressure of the gas. These residual particles were no doubt in part due to the continuation of the distribution between O and L, shown in fig. 3, and probably also to the conversion of He_{++} into He_+ in their passage through the gas, for in the case under consideration the mean free path for capture was only 7.5 times that for loss for the swiftest particles. An estimate of this effect was made by moving the microscope towards O by the width of its field of view and counting the scintillations at that point. When this correction was made, the number fell off according to an exponential law within the limit of experimental error.

The number of particles N_p remaining at a pressure p mm. at 0°C . is given by $N_p/N_0 = e^{-\mu p l}$, where μ is a constant and l cm. the effective length of gas traversed. This length was somewhat less than the actual distance between the source and screen, for a correction was necessary owing to the finite width of the field of view of the microscope. It is obvious that a particle might not be deflected from the field of view if it captured an electron when near the zinc-sulphide screen. The magnitude of this correction depended on the strength of the magnetic field as well as on the width of the field of view, and was easily allowed for. It is clear that the mean free path for loss is given by $1/76\mu$ in terms of millimetres of the gas at N.P.T. For example, for a velocity $\cdot 47V_0$ the number of particles were reduced to half their initial value

for a pressure of air of 1/50 mm. The effective value of l was 13.0 cm. Consequently the mean free path for captures in air was 5/1000 mm. at N.P.T.

The removal of the electron from the He_+ particle corresponds to a process of ionization of the moving particle itself. It is to be anticipated that this ionization should obey laws similar to those found for the ionization of a gas by the swift α particle. This is found to be the case, for the value of λ_2 was approximately proportional to the velocity of the particle between the velocities $.94V_0$ and $.47V_0$. This is in accord with the well-known fact that the ionization produced in a gas by an α particle is inversely proportional to its velocity over this range. This analogy was still further emphasized by comparing the mean free path for loss of an electron in hydrogen and helium as well as in air. It is known that the ionization in hydrogen and helium per unit path is about one-quarter of its value in air for the same velocity. The mean free path in hydrogen was found to be 4 to 5 times longer than in air. The few experiments made with helium indicated that its mean free path was longer than in hydrogen and 5 to 6 times its length in air.

It will be seen that the mean free path for loss is measured in air or other gas, while the ratio λ_2/λ_1 is measured in mica or other solid material. It was, however, found experimentally that the ratio λ_2/λ_1 observed with mica alone, for a velocity of rays of $.47V_0$ changed only slightly when a thin layer of celluloid, aluminium, or silver was placed over the mica plate. The thickness of the layer—of the order of 1 mm. stopping-power for α rays—was sufficient for a new equilibrium to be set up between He_{++} and He_+ particles, but not enough to alter markedly the velocity of the issuing rays. Since little change* was observed for such a wide range of average atomic weight of absorber, we may conclude that the ratio λ_2/λ_1 , if it could be measured entirely in air, would be nearly the same as that observed for mica in which oxygen is an important absorbing constituent. The validity of this relation for all velocities requires further experimental confirmation, but it is probably not seriously in error. The approximate constancy of the ratio λ_2/λ_1 for different elements is a matter of considerable interest, but requires further

* When a thin sheet of gold was placed over the mica, the number of He_+ particles was approximately doubled, indicating that the ratio λ_2/λ_1 does vary appreciably in this case. A more detailed investigation of the variation of this ratio with the atomic weight of the element is being undertaken by Mr. Henderson in the University of Saskatchewan.

verification by a more accurate method than that of counting scintillations.

The values of $\lambda_2/\lambda_1 = N_2/N_1$ for mica were directly measured for three velocities, viz. $\cdot94$, $\cdot76$, $\cdot47V_0$ in a high vacuum, while the mean free path in air for conversion of He_+ into He_{++} was obtained for the same velocities. The results are given in the following table, where the mean free path both for capture and loss is given in terms of mm. of air at N.P.T. :—

TABLE I.

Velocity in terms of V_0 .	λ_2/λ_1 for mica.	Mean free path for loss in air.	Mean free path for capture in air.
$\cdot94$	1/200	$\cdot011$ mm.	2.2 mm.
$\cdot76$	1/67	$\cdot0078$ „	$\cdot052$ „
$\cdot47$	1/7.5	$\cdot0050$ „	$\cdot037$ „

The velocity V_0 of the α particles from radium C is 1.922×10^9 cm.

Over the ranges examined, viz. from $\cdot94V_0$ to $\cdot47V_0$, the ratio λ_2/λ_1 varies very rapidly with the velocity. If we suppose the variation is expressed by V^n , the average value of n from the data obtained is about 4.6, or the ratio λ_2/λ_1 varies roughly inversely as the fifth power of the velocity. Since λ_2 varies nearly as the first power of V , it is seen that λ_1 , the mean free path for capture, varies as $V^{5.6}$, or roughly as the sixth power of the velocity. These relations are only approximate; accurate values will require a large amount of careful counting of scintillations over a wide range of velocity of the α particles.

A number of experiments were also made with thorium C as a source instead of radium C. For this purpose a nickel wire of $\cdot3$ mm. diameter was exposed in a solution of radiothorium. It is well known that the radiation from this source consists of 65 per cent. of α particles of range 8.6 cm. and 34 per cent. of particles of range 4.8 cm. A thickness of mica of 1.1 cm. stopping-power was placed over the source, so the emergent α rays were of range 7.5 and 3.7 cm. respectively. It was possible in a strong magnetic field to resolve completely the midway and main bands due to the two sets of α rays, so that the particles could be independently counted. Unfortunately, with the

active matter available, it was impossible to concentrate sufficient activity on the fine nickel wire to obtain a sufficient number of scintillations per minute for accurate counting in the midway band with the faster particles. The average number was only 6 to 8 per minute in the various experiments. The ratio $\lambda_2/\lambda_1=1/330$ was found for the 7.5 cm. particles, *i. e.* for a velocity $1.02V_0$. The ratio calculated from the results with radium C by means of the power law was about $1/290$. The agreement is as good as could be expected, considering the small number of scintillations which were counted.

It was of interest to note that, although the number of particles in the main band of range 3.7 cm. was only about one-half of those of range 7.5 cm., the number of particles in the corresponding midway bands was nearly in the ratio of two to one. Such a result is to be anticipated from the data previously discussed. There is no evidence that the α particles from thorium C show any difference with regard to frequency of capture and loss from the α particles of radium C of corresponding velocities.

Capture and loss at low velocities.

A large number of experiments have been made to determine the distribution curves of the particles for low velocities in order to estimate the ratio of He_+ to He_{++} over a wide range of velocities from a single curve. One of these distribution curves is shown in fig. 4 corresponding to α particles of emergent range about 4.6 mm. It is seen that the particles composing the midway band A and the main band B are very heterogeneous. The high-velocity edges of these two bands are not so sharply defined as for higher velocities, so that it is difficult to determine directly the mean free path for loss by introducing gas into the apparatus. In addition, since the mean free path for capture and loss is of the same order of magnitude, complications arise from the conversion of He_{++} to He_+ and of He_+ to He_0 in the passage of the rays through the gas.

The following procedure was adopted to compare the relative number of He_+ and He_{++} for different small velocities. A sufficient magnetic field was applied to give a convenient deflexion, generally about 10 mm., of the edge of the midway band. The microscope was fixed at a certain position and the scintillations counted. The current through the magnet was then adjusted to give exactly half the magnetic field. This brought the He_{++} particles over the

same small range of velocity in the field of view of the microscope, and their number was counted. In this way the ratio of singly- to doubly-charged particles was determined over the whole range of velocities available. The advantages of this method of comparison were many. The ratio required of the number in the two bands was directly obtained by counting successively and under identical conditions on the same part of the screen. These conditions are particularly advantageous with weak scintillations where counting is difficult, and the actual number counted is somewhat dependent on the luminosity of the screen and fatigue of the eyes.

The maximum velocity of the particles in the bands was $\cdot 37V_0$. The maximum of the midway band occurred at a velocity $\cdot 32V_0$ and for the main band $\cdot 35V_0$. The singly- and doubly-charged particles were equal in number at a velocity $\cdot 29V_0$. Assuming that λ_1/λ_2 varies as $V^{4.6}$, the calculated velocity for equality in number is $\cdot 30V_0$ —a value in good accord with that observed.

It was possible to count with some certainty down to a velocity $\cdot 22V_0$. Below this velocity the particles were faint and few in number, and difficult to count with accuracy. The results obtained are illustrated in the following table :—

TABLE II.

Velocity.	Observed $N_2/N_1 = \lambda_2/\lambda_1$.	λ_2/λ_1 Calculated values.
$\cdot 47V_0$	$\cdot 133$	$\cdot 133$
$\cdot 32V_0$	$\cdot 53$	$\cdot 68$
$\cdot 29V_0$	$1\cdot 00$	$1\cdot 2$
$\cdot 27V$	$1\cdot 5$	$1\cdot 7$
$\cdot 23V_0$	$3\cdot 0$	$3\cdot 6$

The values for $\cdot 47V_0$ are taken from Table I. for comparison. The calculated values in the third column are deduced from the value for $\cdot 47V_0$, assuming that $\lambda_1/\lambda_2 \propto V^{4.6}$. Considering the wide range of extrapolation and the difficulties of the experiment, the agreement is as good as can be expected, indicating that the velocity law holds approximately over the wide range from $\cdot 23V_0$ to V_0 . Comparing the values of λ_2/λ_1 , viz. $1/200$ for $\cdot 94V_0$, and the value $3\cdot 0$ for $\cdot 23V_0$, the

index of the power law is 4.54. It is thus seen that the ratio of singly- to doubly-charged particles has been examined over a range of more than 600 times. If we assume that the mean free path for loss varies directly as the velocity down to the velocity $\cdot 23V_0$, the mean free path for capture varies in the experiments over a range of about 2500 times.

Undelected particles.

Undelected helium atoms were first noted in considerable numbers in the experiment corresponding to fig. 3, where the maximum velocity of the α particles was $\cdot 47V_0$. The scintillations were for the most part faint, and were about $1/140$ of the number of α particles in the main band. In the experiment, illustrated by fig. 4, for still lower velocities the number of undelected particles was relatively greater, corresponding to about $1/40$ of the total number of α particles.

No doubt the undelected particles mainly arise from the low-velocity particles which carry a single charge. From the average brightness of the scintillations, I should judge the mean velocity of the particles lay between $\cdot 25V_0$ and $\cdot 30V_0$, but a number of very faint particles corresponding to very low velocities were noted under exceptionally good conditions for counting. No doubt the neutral particles are very heterogeneous in velocity, but, from the nature of the experiments, it is difficult to estimate their distribution with velocity.

By introducing a small quantity of gas into the apparatus, the number of particles in the neutral band diminished and practically disappeared for a pressure of air of about $3/100$ mm. The actual stopping-power of this pressure of residual gas is only about $1/160$ mm. of air at N.P.T., and thus is much too small to reduce seriously the velocity of the particles.

It seems clear that the disappearance of the neutral band is due to the conversion of neutral into singly-charged helium atoms. Some experiments were made to estimate the mean free path in air of the conversion He_0 to He_+ . The observations are difficult on account of the weakness of the scintillations, but it was estimated that the mean free path for conversion of He_0 into He_+ was about $1/100$ mm. or about $1/5$ of the mean free path for conversion of He_+ into He_{++} for a velocity $\cdot 47V_0$. No certain difference was noted in this respect between the neutral particles produced under the conditions illustrated in figs. 3 and 4.

Singly-charged particles from naked sources.

It was of great interest to examine whether the bare platinum source, without any mica covering, gave any singly-charged helium atom. The observations were made rapidly after the wire was introduced into the apparatus, for under such conditions the general contamination due to the bare source is not serious. It was found that the number of singly-charged particles was about the same in number as if the wire had been covered with a thickness of mica of 3 or 4 mm. stopping-power to give the equilibrium distribution. This was a surprising result when it is considered that the mean free path for capture for such high-velocity particles is about 3 mm. of air and the amount of active matter is too small to form even a film of one molecule thick over the surface of the wire. These He_+ particles could not be due to the heterogeneity of the rays produced by the source, which has already been referred to, for only the swiftest α particles were counted by the microscope. When the wire is exposed to the emanation, the radium A atoms are deposited on the surface, and some of the radium B atoms are thus driven into the wire by recoil. Consequently, some of the α particles escaping from radium C have to pass through a small thickness of platinum. Calculation shows that this thickness is much too small to set up an equilibrium between He_+ and He_{++} . However, in order to test the matter further, a source of radium C was obtained by electrolysis on nickel. In this case the radium C is deposited directly on the surface of the nickel, and the effect due to recoil should be absent. Again, the number of He_+ was about the equilibrium value.

It is very difficult to believe that these He_+ particles come directly from the nucleus; and, even if this be assumed, it is a curious coincidence that the number should be about that required for equilibrium between He_+ and He_{++} in their passage through mica. We are driven to the conclusion that at any rate a partial equilibrium is set up by the passage of the α particle through the dense distribution of the electrons round the nuclei from which they are expelled. It is well known that the collisions due to an α or β particle in escaping from the nucleus of an atom appear to be much more effective than if the particle passes into the atoms from the outside. It may well be that some of the particles may gain or lose an electron several times before they escape from the parent atom, and thus an approximate equilibrium may be set up between the singly- and doubly-charged

particles. For example, it is to be expected that this interchange of electrons would most readily occur in the groups of electrons whose orbital velocity is about the same as the velocity of the α particle.

The effect of gas in the path of the α particles.

Consider an experiment similar to that illustrated in fig. 4, where A, B, and C represent the distribution of He_+ , He_{++} , and He_0 in a vacuum. On adding gas, these three bands disappear and are replaced by a single comparatively narrow band shown in D. To obtain this band, the pressure of air in the chamber was 1.1 mm., corresponding to a stopping-power of .23 mm. of air for the α particle. Since the mean free path for capture for the highest velocity of particles present, viz. $.37V_0$, is probably about .008 mm., it is seen that the average number of captures and losses in the air for an α particle of this velocity is about 30, and still more for the slower particles. When the captures of an α particle in traversing the gas are as numerous as this, each α particle of definite velocity in a magnetic field is deflected as if it carried a charge between e and $2e$, the actual magnitude depending on the ratio of the mean free paths for capture and loss.

It can be readily calculated from the observed distributions with velocity of He_+ and He_{++} in a vacuum, that the particles after traversing the gas should be mainly concentrated in a comparatively narrow band such as is shown in curve D.

Consider α particles of velocity V whose mean free paths in the gas are λ_1 and λ_2 for capture and loss respectively. Since there are many interchanges of charge in traversing the gas, the magnetic deflexion will correspond to particles of velocity V of which the average charge is

$$\frac{\lambda_1 2e + \lambda_2 e}{\lambda_1 + \lambda_2} \quad \text{or} \quad e \left(1 + \frac{\lambda_1}{\lambda_1 + \lambda_2} \right).$$

The magnetic deflexion will thus be proportional to

$$\frac{e}{V} \left(1 + \frac{\lambda_1}{\lambda_1 + \lambda_2} \right).$$

From the experimental data for λ_2/λ_1 given in Table II., and adding the value for the velocity $.37V_0$, it can be calculated that the magnetic deflexion of α particles of velocities $.37, .32, .29, .27, .23V_0$ is proportional to 483, 516, 517, 518, 543 respectively in arbitrary units. Now, the velocity of the α particles in the main beam B lies mainly between the

velocities $\cdot 23$ and $\cdot 37V_0$. It is thus seen that the deflected band with gas in the vessel should be confined within a much narrower range of velocity than the main or midway band in a vacuum. This, as we have seen, is found to be the case experimentally. From the calculations, it seems clear that the concentration of particles should be very marked for a very narrow pencil of α rays. Whatever the concentration, the band cannot be narrower than the normal width of the beam in a vacuum with no magnetic field. It is intended later to examine the concentration with very narrow beams, as it may be expected not only to afford a definite test for the reliability of the data for capture and loss at low velocities, but also to throw light on the question whether one α particle differs from another with regard to frequency of capture or loss. This possibility has been suggested by P. Kapitza * as an explanation of the different curvatures observed in α -ray tracks when acted on by intense magnetic field.

This concentration effect, which is so intimately connected with the frequency of capture and loss at low velocities, gives a very simple but direct method of testing the important question whether an α particle captures electrons in hydrogen as well as in air. Since the mean free path for loss in hydrogen is about five times as long as in air, hydrogen was introduced into the vessel at a pressure of about 5 mm., equivalent to the pressure of 1 mm. used for air. Under such conditions the curve for hydrogen was very similar to that obtained for air, and showed a similar concentration. This affords a definite proof that the α particle captures electrons in hydrogen and that the ratio of the mean free path for capture to that for loss is of the same order as for air. This result will be seen to be of some importance in the discussion of the mechanism of capture.

Number of interchanges.

From the data given in this paper, it is clear that the interchange of charges presented by $\text{He}_{++} \rightleftharpoons \text{He}_+$ is predominant down to a velocity $\cdot 29V_0$ where the number of H_+ and H_{++} are equal. Below this velocity the interchange $\text{He}_{++} \rightleftharpoons \text{He}_+$ begins to be important, and no doubt becomes predominant for low velocities of the α particle. It is clear also that the interchanges of charge of the α particle are very numerous in its flight. A rough estimate of the number of

* P. Kapitza, Camb. Phil. Soc. xxi. p. 511 (1923).

captures between any specified velocities of an α particle can be made in the following way. It is convenient to express the velocity of the α particle and its mean free path for capture and loss as multiples of the corresponding values for the maximum velocity V_0 of the α particle from a bare dium C source.

If $x=V/V_0$, the mean free path λ_1 for capture is given by $\lambda_1/L_1=x^{5.6}$ where L_1 is the mean free path for capture for a velocity V_0 . From the cube law connecting the velocity of an α particle with its range, $R=R_0x^3$ where R is the range of α particles of velocity V , and R_0 the maximum range for velocity V_0 . Differentiating, $dR=3R_0x^2dx$, the number of captures in the distance dR ,

$$= \frac{dR}{L_1} = \frac{3R_0}{L_1} x^{-3.6} dx.$$

The total number of captures between velocities x_1 and x_2

$$= \frac{3R_0}{2.6L_1} (x_2^{-2.6} - x_1^{-2.6}).$$

Take $L_1=3.1$ mm., $R_0=7.06$ cm., the number of captures between velocities V_0 and $.29V_0$ is seen to be 630. This is an over-estimate, for we must remember that every capture is followed by a loss. By taking account of the variation of mean free path for loss over the path, I estimate that on the average 590 captures occur from the beginning of the range of the α particle to the velocity $x=.29$ where the mean free paths for capture and loss are equal. It can also be shown that on the average for the range traversed, viz. 6.89 cm., the α particle remains doubly charged for a total distance of 6.39 cm. and singly charged for a distance .50 cm. Too much stress must not be laid on this calculation, for it assumes the accuracy of Geiger's rule connecting range and velocity, viz. $V^3 \propto R$. Blackett * has recently shown that this law breaks down in the last centimetre of the range, and the experimental results are more nearly expressed by a relation of the form $V^{-1.5} \propto R$. It follows that the range of particles falls off more slowly with velocity in the last centimetre than is calculated on Geiger's rule, and consequently the number of captures have been underestimated. Since the α particle at velocity $.29V_0$ makes 300 captures and losses per mm. of path, it is easily seen that the change in the law of absorption will cause a considerable increase in the total number of captures. In addition, the mean free path for

* Blackett, Proc. Roy. Soc. A, cii. p. 294 (1922); ciii. p. 62 (1923).

conversion $\text{He}_0 \rightarrow \text{He}_+$ has been shown to be small (see p. 291). We shall not be much in error if we suppose that the interchange of charges must occur several thousand times in all during the flight of the α particle. It is probable that the number of captures, for complete absorption of the α particle, is of the same order for all the elements including hydrogen, though no doubt the total number will vary somewhat for the different elements probably in the same sort of way that the total ionization of the α particles is known to vary.

When we consider the frequency of capture or loss of electrons by the α particle, we should not expect to notice any appreciable change in the power of penetration of particles in the main, midway, or neutral bands, provided we compare particles of identical velocity. Henderson (*loc. cit.*) made some comparisons of this kind, but with indefinite results. If any marked difference in penetration were to be observed, it would afford strong evidence of some individual differences in the α particles, such as has been suggested by Kapitza, with regard to capture or loss or both.

Comparison with Positive Rays.

Observations on the capture and loss of electrons by the α particle have been studied in this paper between velocities V_0 and $\cdot 23V_0$, *i. e.* between $1\cdot922 \times 10^9$ and $4\cdot4 \times 10^8$ cm. per second. The phenomena of capture and loss shown by the α particle are very similar to those shown by the positive rays in a discharge-tube. The theory of this has been worked out by W. Wien, and an interesting account of the various investigations made to determine the mean free path of charged hydrogen atoms and neutral hydrogen atoms in various gases have been given in a recent paper by E. R. Rüchardt*. The maximum velocity of the hydrogen atoms used in his experiments was about $2\cdot26 \times 10^8$ cm. per second corresponding to a P.D. of 35,000 volts. The experiments on the α particle have thus been made at much higher velocities than for hydrogen atoms, and the highest velocity examined by Rüchardt is only one-half of the lowest velocity of the α particle studied in the present paper. In order to obtain velocities of H_+ equal to the α particles from radium C, an accelerating potential of 2.5 million volts would be necessary. From the results of Rüchardt on hydrogen rays it can be deduced that the mean free path for capture and loss in nitrogen is about the same, *viz.* about $1/2000$ mm. at N.P.T.

* *Ann. de Phys.* lxxi. p. 322 (1923).

for a velocity of 2.26×10^8 cm. per second. This corresponds to a velocity $\cdot 12V_0$ in terms of the α particle.

Now, it is to be expected that the interchange $\text{He}_+ \rightleftharpoons \text{He}_0$, if governed mainly by velocity, must behave very similarly to the interchange $\text{H}_+ \rightleftharpoons \text{H}_0$, with the difference that the ionizing potential of helium is higher, about 24.5 volts, than the ionizing potential of hydrogen, 13.5 volts. We should thus expect from the experiments on hydrogen rays that the mean free path of He_+ and He_0 should be equal for a velocity somewhat higher than in the case of hydrogen rays. I estimate its probable value to be $\cdot 16V_0$.

In the case of the α particles, the actual velocity for equality has not so far been measured, but the rough results obtained of the relative numbers of He_0 and He_+ are not inconsistent with such a value. It is of interest to note that the mean free path for the conversion of He_0 into He_+ was estimated to be about 1/1000 mm.

It is not to be expected that the variation with velocity of the mean free paths for capture and loss, observed for hydrogen rays, should follow the relations observed for swift α rays. From the data given by Rüchardt for hydrogen rays, no very definite conclusions can be drawn on the variation with velocity of the mean free paths in various gases. In the table, however, given in his paper (p. 409), referring to the passage of hydrogen rays through oxygen, it can be deduced that the ratio of the mean free paths for capture and loss varies roughly as V^{+6} for a range of velocities corresponding to 24,500 and 36,800 volts. This law is the same as we have observed for high-velocity α particles, but the agreement may be only accidental, since the corresponding data for nitrogen at lower velocities does not accord with such a relation.

Discussion of results.

When an α particle captures an electron, it presumably falls in the majority of cases into the same orbit round the helium nucleus which characterizes an ionized helium atom. The ionization potential under these conditions is believed to be 54 volts. When the α particle with the attendant electron passes through the atoms of a gas in its path, it will not only ionize the gas, but will occasionally be itself ionized, i. e. will lose its attendant electron. We shall see that the mean free path for loss calculated on these assumptions is of about the magnitude observed experimentally. In making

the calculation, it is necessary to draw a sharp distinction between the primary and secondary ionization* produced by an α particle. This point has been discussed recently by R. H. Fowler†. Consider for simplicity the ionization in hydrogen. Corresponding to the maximum velocity V_0 of radium C, the α particle produces 528 ions per mm. of path, and of these only $1/4 \cdot 4$, i. e. 120, are primary. Now, the mean free path in hydrogen for loss of an electron from He_+ is for this velocity about .060 mm. In this distance, where one He_+ atom is ionized the α particle produces 7.2 primary ions. Taking the ionization potential of hydrogen as 16 volts and for He_+ as 54 volts, the numerical relation observed is in fair accord with calculation. In order to calculate the chance of ionization of the He_+ atom, it is simplest to suppose that the He_+ atom is at rest and the hydrogen molecules are carried past it with the velocity of the α particle. The probability of ionization by the component electrons and by the hydrogen nuclei are determined separately. There is still some uncertainty as to the relative primary ionization of electron and of a hydrogen nucleus, so that the calculated results are not as definite as could be wished.

It seems clear, however, that the mean free path for loss is in good general agreement with theory for all velocities of the α particles where observational data are available. It is of interest to note that the agreement of theory with calculation indicates that in most cases the electron captured by an α particle falls rapidly into the lowest quantum orbit and does not appear to circulate in an orbit of high quantum number, i. e. of low ionization potential, even for the short interval of time required to traverse the short distance corresponding to the mean free path for loss.

While we can thus offer a quantitative explanation of the observed mean free path for loss of an electron, the inverse problem of the capture of an electron by a swift α particle presents many difficulties. Indeed, it was for a long time implicitly assumed that the α particle could only capture an electron near the end of its range when its velocity was much reduced.

Before considering possible explanations of the phenomena of capture for high-speed α particles, it is desirable to emphasize two important points. We have seen that the

* The α particle often liberates an electron from an atom with sufficient velocity to produce several new pairs of ions. These are included in the term secondary ionization.

† Fowler, Proc. Camb. Phil. Soc. xxi. pp. 21, 532 (1923).

equilibrium between doubly- and singly-charged α particles is very little altered by the nature of the material traversed by the α particle. We know, however, that the ionization per unit path in a gas, and hence the frequency of loss of an electron from He_+ , increases rapidly with the mass of the atoms of the gas. Since the frequency of capture is nearly proportional to the frequency of loss over a wide range of atomic weight, it is clear that the fundamental processes involved in capture must be intimately connected with those taking place in the ionization of a gas by an α particle. In a sense, the process of capture is the inverse of the process of ionization where an electron is removed from an atomic system by a passing α particle.

It has been suggested that the process of capture may be connected with the removal of strongly-bound electrons from the nucleus, where a comparatively large amount of energy must be given to the electron to cause its escape from the atom. For example, in nitrogen or oxygen the ionization potential of the K electrons is of the order of 500 volts. While no doubt for low velocities of the α particles the frequency of both capture and loss is to some extent dependent on the strength of the binding of the electron by the nucleus of an atom, there is no evidence that this factor is of importance in the capture of an electron by high-velocity particles. This view is substantiated by the experimental proof that capture occurs readily in hydrogen although its ionization potential is about 16 volts.

In the actual experiments, the α particle is shot at a high speed through molecules which for all practical purposes may be supposed to be at rest. For convenience of discussion, it is sometimes preferable to suppose that the α particle is at rest and the molecules stream by it with a velocity equal and opposite to that of the α particle. We shall first of all consider this hypothetical case of capture of a swift electron by an α particle at rest. The maximum velocity of the α particle from radius C corresponds to a 1040-volt electron—*i. e.*, it is equal to the velocity gained by an electron in falling freely through this difference of potential. For purposes of discussion, it is often very convenient to speak of an electron having a velocity or energy of a 1040-volt electron. Since the ionization potential of the outer electrons of the simple gases varies between 11 and 25 volts, we see that the energy for removal of an outer electron is small compared with that of a 1000-volt electron, and thus cannot seriously influence capture for a swift α particle. On the ordinary theory of a non-radiative

collision between an isolated electron and an α particle. capture can never occur. In practice, however, the electron is always bound to a nucleus, and the collision is not between the isolated charged particles, but involves the interaction of three or more charged systems. In order for capture to occur, the electron must lose in some way the greater part of its energy of translation. It is natural to suppose that this loss of energy occurs by radiation. On such a view, one method of capture of a swift electron by a nucleus may be regarded as the converse of the photo-electric effect in which radiation falls on matter and electrons are ejected. In the case under consideration, swift electrons are shot towards a charged nucleus, and an occasional electron is captured with the emission of its surplus energy in the form of radiation. While it is quite probable that this is one of the processes which lead to the capture of electrons, this conclusion is not of much help in giving us a physical insight into the processes of capture involved in the direct case where a fast α particle collides with an electron in an atom nearly at rest. It is clear that if an electron is captured and moves with the α particle, it must in some way acquire an energy of translation corresponding to that of an electron moving with the velocity of the α particle. For example, capture by a 1000-volt α particle will only be possible if the electron in some way gains energy corresponding to the order of 1000 volts. It is thus natural to suppose that capture is connected with a collision between an α particle and an electron which gives the latter a velocity within a certain range of the velocity of the α particle. If the electron after the collision makes an angle θ with the direction of motion of the α particle, its velocity u is equal to $2V \cos \theta$, where V is the velocity of the α particle. If $u > V$, $\theta < 60^\circ$. It is likely, however, that capture can only occur if the electron ultimately is shot forward within a small angle of the direction of the α particle with a velocity not very different from that of the α particle. Since it is clear that capture does occasionally take place as the result of an encounter of an α particle with a single atom, we are driven to conclude that the interactions of the other charged bodies involved are intimately connected with the mechanism of capture. For example, it is easily seen that the ultimate direction of escape of the electron may depend on a second collision with the nucleus or other electron before escape from the atom. The velocity of the electron is not seriously altered by a nuclear collision, but will always be reduced by a collision with another electron.

Following this line of argument, we can see in a general way that electrons of velocity within a certain range of that of the α particle may occasionally be captured, if their velocity and direction can be altered by a second collision. No doubt the idea of two successive collisions in the atom, each more or less independent of each other, is somewhat artificial. It is much more likely that capture results from what may be regarded as a single encounter between an α particle and two or more charged bodies, and it would prove difficult to separate the factors involved. The whole problem is too involved and complicated to attempt to reduce to calculation, but it may be of interest to give a few estimates of the order of magnitude of the quantities involved.

Suppose an α particle of mass M , charge E , and velocity V collides with an isolated electron of charge e and mass m which is deflected through an angle θ with the original direction of the α particle. With the ordinary notation,

$$p = \mu \tan \theta,$$

where

$$\mu = \frac{Ee}{mV^2}.$$

If the α particle passes through a thickness t of gas containing n electrons per c.c., the number of electrons q which are deflected between the angles 0 and θ is given by

$$q = \pi p^2 \cdot n \cdot t = \pi n t \mu^2 \tan^2 \theta.$$

First, consider the α particles from radium C of velocity 1.922×10^9 cm. per sec. passing through nitrogen at N.P.T. The mean free path for capture is about 3 mm. for this velocity, and

$$\mu = 1.37 \times 10^{-10}.$$

Taking 7 electrons per atom,

$$n = 3.8 \times 10^{20}, \text{ and for } t = .3 \text{ } q = 6.7 \tan^2 \theta.$$

Between $\theta = 0$ and $\alpha = 60^\circ$, *i.e.* between velocities $2V$ and V ,

$$q = 20,$$

$$\text{and } p \text{ for } 60^\circ = 2.37 \times 10^{-10} \text{ cm.}$$

On this calculation, 1 in 20 of the electrons ejected with velocity equal or greater than that of the α particle is captured by it. If an electron can be captured of energy as low as 900 volts, q becomes 28.

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For a velocity of α particles $\cdot 47V_0$ (230 volts), the value of mean free path for capture $t = \cdot 037$ mm. For electrons shot out between 0 and 60° for this case $q = 5\cdot 0$, or one in five collisions is effective in capture. If we suppose the laws of capture hold down to a velocity $\cdot 22V_0$ (50 volts), each collision which gives to an electron more than 50 volts energy results in capture. In this calculation, no correction has been made for the energy required to ionize an atom. No doubt this factor is of importance for such low velocities.

It may be of interest to look at this problem in a somewhat different way. Suppose it be assumed that all electrons are captured that have energies lying between $E + e$ and $E - e$. On the simple collision theory, this is equivalent to the statement that all electrons deflected between angles θ_1 and θ_2 with the direction of the α particles are captured. If E_0 be the energy of an electron moving with the speed of the α particle, then

$$E + e = 4E_0 \cos^2 \theta_1$$

and

$$E - e = 4E_0 \cos^2 \theta_2.$$

The number of collisions which deflect electrons between θ_1 and θ_2 is given by

$$\pi n t \mu^2 (\tan^2 \theta_2 - \tan^2 \theta_1).$$

The value

$$\tan^2 \theta_2 - \tan^2 \theta_1 = \sec^2 \theta_2 - \sec^2 \theta_1$$

$$= \frac{8E_0 e}{E^2 - e^2} = \frac{8e}{E_0} \left(1 + \frac{e^2}{E_0^2} + \dots \right),$$

if we suppose that the mean value of the energies $E = E_0$ and e/E is small.

If we suppose e to be a constant for all velocities, then since $1/E \propto 1/V^2$ and μ^2 includes the term $1/V^4$, the number of captures per unit path varies as V^{-6} —a deduction in good accord with experiment.

Using the data for capture already given for rays from radium C of maximum velocity 1040 volts, it follows that $e = 19$ volts. On this view the frequency of capture would be in agreement with experiment if all electrons were captured between energies 1021 and 1059 volts. This is equivalent to the assumption that for this speed, only those electrons are captured which are shot within an annular ring of each electron for which the values of p lie between $2\cdot 40 \times 10^{-10}$ and $2\cdot 34 \times 10^{-10}$ cm. If it be assumed, as seems probable, that only a fraction of such electrons are

captured, the value of e must be correspondingly increased. If necessary, the formula may be corrected to take account of the energy ω required for ionization. In such a case, E should be replaced by $E_0 + \omega$.

While these calculations give a formal agreement with the results of experiment, they do not offer any definite explanation of the mechanism of capture under the conditions postulated, and in that sense are somewhat artificial. As already pointed out, a collision which results in capture must involve at least three bodies, and is thus not easily amenable to calculation. Under these conditions, it does not appear profitable at this stage to consider the question in more detail. This is all the more so, as in an accompanying paper* Mr. R. H. Fowler has been able to give not only a qualitative, but to a fair approximation a quantitative explanation of the frequency of capture of an electron by an α particle. This is based on certain general deductions from the laws of dissociative equilibrium, which demand that any process such as ionization must be balanced by an analogous reverse process (in this case capture). This must be done in such a way that the rate of the frequencies of the two processes is uniquely determined without any further knowledge of the details of the mechanism, by the condition that the law of dissociative equilibrium must be preserved unaltered.

I desire to express my thanks to my assistant, G. A. Crowe, for his help in these experiments, and to Mr. Ellis, Mr. Blackett, and Mr. Barton for their assistance in counting scintillations.

Cavendish Laboratory,
Dec. 1923.

XXV. *Damped Vibrations.*

By C. F. JENKIN and W. N. THOMAS †.

IN the Phil. Mag. for July 1922 Mr. H. S. Rowell describes a simple method of plotting the damped harmonic motion of a system when the damping force is constant. The figure illustrating his paper is, however, a little misleading, since it corresponds to one of the particular initial displacements which will allow the system to come to rest in the central position. In general the

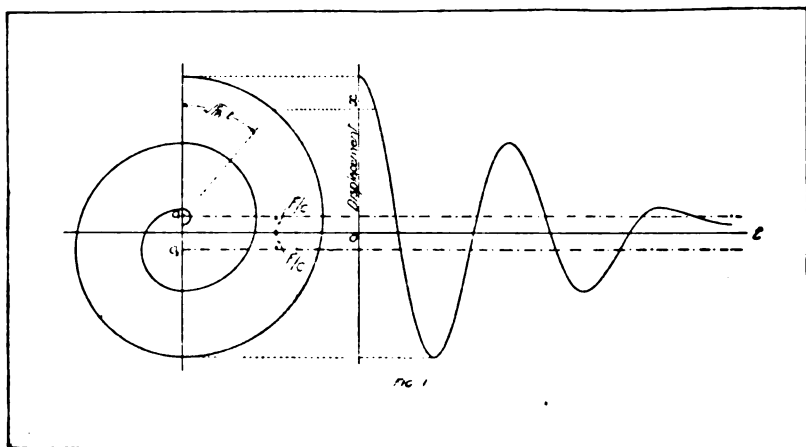
* *Infra*, p. 416.

† Communicated by the Authors.

system may come to rest in any position between the two limiting lines in the diagram. The general case is shown in fig. 1 below. The equation to motion is

$$m\ddot{x} + cx \mp F = 0.$$

Fig. 1.



The solution is (as Mr. Rowell shows)

$$x = A \cos \left(\sqrt{\frac{c}{m}} \cdot t + \epsilon \right) \pm \frac{F}{c},$$

where A is a constant which changes each half period. The value of A for the first half period is (if the initial velocity is zero)

$$A = \text{Initial displacement} - \frac{F}{c}.$$

For the second half period

$$A = \text{Initial displacement} - \frac{3F}{c},$$

and so on. $\epsilon = 0$ if the initial velocity is zero.

The displacement graph is drawn by projection from the series of semicircles drawn round alternate centres O_1, O_2 , spaced $\frac{2F}{c}$ apart. The oscillations continue till one of the semicircles finishes within the distance $\pm \frac{F}{c}$ from the central position.

Mr. Rowell's method may be extended to plot the motion when there is both fluid friction (proportional to the velocity) and solid friction (constant).

The equation of motion is

$$m\ddot{x} + b\dot{x} + cx + F = 0.$$

The solution is

$$x + \frac{F}{c} = Ae^{-\frac{b}{m} \frac{t}{2}} \cos (nt - \epsilon),$$

where

$$n = \frac{1}{2} \sqrt{\frac{4c}{m} - \left(\frac{b}{m}\right)^2},$$

and

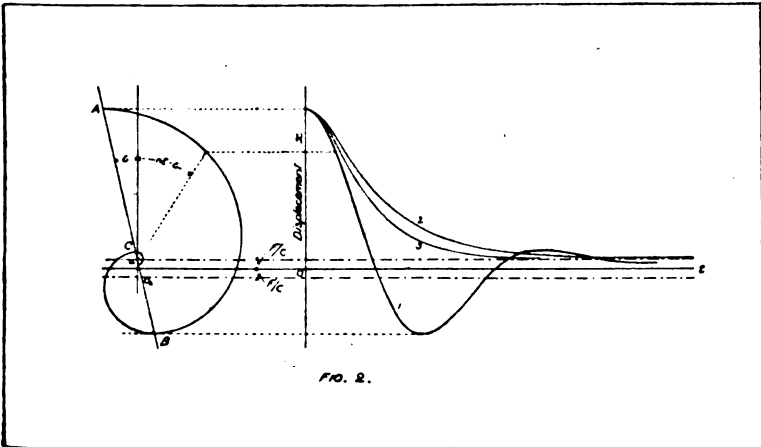
$$\epsilon = \tan^{-1} \frac{b}{2mn},$$

the initial velocity being assumed to be zero.

A is again a constant, changing each half period. Its initial value is given by

$$A \cos \epsilon = \text{initial displacement} - \frac{F}{c}.$$

Fig. 2.



The construction of the graph is shown in fig. 2. It is drawn by projection from the series of equiangular spirals AB, BC, etc. drawn round alternate centres O_1, O_2 . (These replace the semicircles in Mr. Rowell's case.) The points A, B, C, &c., lie on a sloping line, making an angle $\epsilon = \tan^{-1} \frac{b}{2mn}$ with the axis OX. The tangents to the spirals

at A, B, C, &c., are all horizontal, and the points A, B, C, etc., project into the highest and lowest points in the displacement graph.

The oscillations continue till one of the spirals finishes within the distance $\pm \frac{F}{c}$ from the central position (as before).

If the fluid friction exceeds a certain value

$$\left[i. e. \text{ if } \left(\frac{b}{m} \right)^2 > \frac{4c}{m} \right]$$

the motion ceases to be oscillatory and becomes logarithmic. A logarithmic graph is shown in curve 2, fig. 2. The graph

for the critical case $\left[\left(\frac{b}{m} \right)^2 = \frac{4c}{m} \right]$ is shown by curve 3, fig. 2.

Neither of these curves presents any difficulty; they are asymptotic to the line $x = \frac{F}{c}$.

XXVI. *The Absence of Ionization by Electrons with Speeds comparable with that of Light.* By W. F. G. SWANN, A.R.C.S., D.Sc., Professor of Physics in the University of Chicago*.

1. *Introduction.*

THE main interest of the problem here discussed lies in its relation to certain types of theories of the earth's electric charge, in which the replenishment of the charge lost by conduction through the atmosphere comes about in virtue of the agency of high-speed electrons shot into the earth from outside. In the earliest form of such theory, proposed tentatively by G. C. Simpson in 1904†, the electrons come from the sun. In a more recent theory proposed tentatively by the writer they are shot out from the atmosphere as a result of a sort of radioactive disintegration‡; and, in a still more recent theory proposed by the writer§, and independently by von Schweidler||, they are shot out

* Communicated by the Author. Presented at the Christmas meeting of the American Physical Society, 1922.

† "A Theory of the Cause of Atmospheric Electricity," 'Nature,' vol. lxix. p. 270 (1904).

‡ Carnegie Institution of Washington Year Book, 1915.

§ Phys. Rev. vol. ix. pp. 555-557 (1917). Also Journal of the Franklin Institute, vol. clxxxviii. pp. 577-606 (1919).

|| Akad. Wiss. Wien. Ber. vol. cxxvii. 2a, pp. 515-533 (1918).

from the atoms of air through the agency of that so-called penetrating radiation which, supposedly coming from the outer regions of the atmosphere or from some external source, has been invoked for the purpose of accounting for the ionization known to occur in closed vessels freed from radioactive air.

In all such theories the following fundamental difficulty presents itself. The maintenance of the earth's charge necessitates the assumption of an entry of electrons to an extent which amounts, on the average, to 1500 electrons per square centimetre per second. Now, it is a well-known fact that, in the case of electrons travelling with speeds 95 per cent. of that of light, each electron produces about 40 ions in each centimetre of its path; so that, on this basis, we should expect a rate of production of about 40×1500 , i. e. 60,000 ions per c.c. per second near the earth's surface, on account of the high-speed electrons; whereas ions are produced to only one ten-thousandth of this amount, and such ions as are produced may be satisfactorily accounted for by other causes. The object of the present paper is to seek a loophole of escape from this difficulty. The mechanism of the ionization will be discussed in terms of the classical dynamics. This is perhaps a weakness at the present time, when, through the developments of the quantum theory, our ideas as to how a field takes hold of an electron are in such a transitory state; but, since the quantum theory does not yet speak with completeness on this point, it is perhaps not out of place to derive some comfort from showing that even the classical theory may be made to indicate an avenue of escape from the difficulties presented by the large ionization which a superficial view of the situation would suggest as a result of the influx of high-speed electrons to the earth. In what follows, the discussion of fine points, and mathematical details, will be relegated to an appendix at the end of the paper.

2. *Preliminary Formulation of the Theory.*

Suppose that an electron is situated within an atom, and that another electron of high speed, which we shall distinguish by calling it a corpuscle, passes near to the electron. As the corpuscle describes its orbit it will communicate energy to the electron, and will eject it from the atom if the energy communicated is sufficient. Such a theory of ionization was suggested originally by Sir J. J. Thomson*, and was later elaborated by N. Bohr†. The

* Phil. Mag. ser. 6, vol. xxiii. pp. 449-457 (1912).

† Phil. Mag. ser. 6, vol. xxx. pp. 581-612 (1915).

greater the velocity of the corpuscle, the shorter the time during which the electron has opportunity to receive momentum from it; so that the efficiency of the corpuscle as regards its power to hurl the electron out of the atom diminishes with its velocity, and would, as a matter of fact, become zero if the corpuscle could attain an infinite velocity. The velocity of the corpuscle cannot attain a value greater than that of light, however; so that, as regards this effect, there is not very much reduction in ionizing efficiency from, say, 95 per cent. of the velocity of light, where the ionization has been measured, to the velocity of light itself*. As the velocity of light is approached, however, another phenomenon comes in. The field of the corpuscle does not remain uniformly distributed, but, in accordance with ordinary electrodynamical principles, it crowds up more and more towards the equatorial plane of the corpuscle's motion. The time which the corpuscle has for acting effectively on the electron is therefore reduced still further on this account, but the intensity of the field during that time is correspondingly increased; and it turns out, as has been shown by N. Bohr †, that if we take nothing else into consideration, the energy communicated to a free electron by

* The simple theory gives the ionization per centimetre of path as inversely proportional to mV^2 , where V is the velocity of the corpuscle and m the electronic mass. For slow velocities, $\frac{1}{2}mV^2$ is the kinetic energy, so that the statement is made that the ionization per centimetre of path is inversely proportional to the kinetic energy. Von Schweidler (*Akad. Wiss. Wien Ber.* vol. cxxvii. 2 a, pp. 515-533, 1918), taking this statement, substitutes for $\frac{1}{2}mV^2$ the relativity expression

$$m_0c^2 \left\{ \left(1 - \frac{V^2}{c^2} \right)^{-\frac{1}{2}} - 1 \right\}$$

for the kinetic energy, which becomes infinite as V approaches c , the velocity of light. He thus concludes that the ionization should diminish indefinitely as the velocity of the corpuscle approaches that of light. It would appear, however, that the conclusion cannot be substantiated on this basis: for a detailed examination of the elements of the calculation will show that the $\frac{1}{2}mV^2$ occurs in the original expression not really as the representative of the kinetic energy of the corpuscle, nor of anything which should attain an infinite value as V approaches the velocity of light. Indeed, the m in that expression is really the representative of the mass of the electron which is *being ejected* from the atom, while the V is the velocity of the corpuscle. The occurrence of V^2 in the denominator of the expression for the ionization per centimetre of path is closely bound up with the fact that the time during which the corpuscle is in effective proximity to the atom diminishes with the velocity. A fuller analysis of the situation is given in Appendix, Note 1.

† *Phil. Mag.* ser. 6, vol. xxx. pp. 581-612 (1915). See also Appendix, Note 1.

the passage of the corpuscle will be unaffected by this concentration of the lines of force towards the equatorial plane*.

There is, however, one very important consideration which must be taken into account. The impartation of even a small amount of energy to an electron in a very short time results in a large radiation of energy. In fact, if the velocity of an electron increases with acceleration f , the rate of radiation is proportional to f^2 †. If, then, f is infinite, while $\int f dt$, the velocity gained, is finite, it is obvious that $\int f^2 dt$ will be infinite. Now, the nearer the velocity of the corpuscle approaches the velocity of light, the more suddenly does the corpuscle communicate to the electron such energy as it imparts; and, as will be shown in greater detail below, the situation is such as is approximately symbolized by the following:—In the case of a corpuscle moving with a velocity approximating that of light (say 95 per cent. of that of light), but not so closely as to involve radiation considerations, it turns out, as may readily be shown from Sir J. J. Thomson's theory, that the corpuscle must approach an electron of an oxygen atom within 0.7×10^{-10} cm. in order to give to that electron enough energy to insure its ejection from the atom—an energy corresponding to the fall of the electronic charge through 15.5 volts. If the minimum distance of approach is less than this amount, the energy imparted to the electron will be greater; if it is more, the energy imparted will be less. It is, however, possible to assign to the corpuscle a velocity so high that, *irrespective of the distance of approach*, if we should suppose it to transmit to the electron an energy corresponding to 15.5 volts, we should lead ourselves to the impossible conclusion that the electron's acceleration would be so large that the energy radiated by it in acquiring its velocity would be greater than the work done on it by the corpuscle. Thus, corpuscles having the velocity in question, or any higher velocity, would be unable to eject an electron from the atom of oxygen.

* When the electron is bound in the atom, the considerations are modified, as shown by Bohr's calculations; but a situation such as that under discussion, where the time of action of the force on the electron is exceptionally short, is, of all cases, the one most favourably adapted to the neglect of binding forces on the electron.

† For very rapid changes of acceleration, this statement involves assumptions which are discussed in Appendix, Note 2.

3. *Mathematical Formulation of the Problem.*

For the corpuscular speeds concerned, where the mass is so many times the mass for small velocities, the corpuscle will suffer but little deviation in passing the electron, and it will suffice to regard its path as straight for the purpose of calculating the force which it exerts upon the electron as a function of the time. Moreover, in calculating this force, we shall regard the electron as a *point* charge. The latter assumption presents certain difficulties concerned with the variation of the field of the corpuscle over the volume of the electron and with the inertial and radiation reactions. A discussion of these is given in Appendix, Note 2.

According to the classical electrodynamics, an electron of charge e , moving with acceleration f , radiates energy at a rate $2e^2 f^2 / 3c^3$, where c is the velocity of light.

If F is the force on the electron at any instant, v its velocity at that instant, and v_0 the maximum velocity which it attains, we always have

$$v_0 F \geq v F > \frac{2e^2 f^2}{3c^3}, \quad \dots \dots (1)$$

since the rate of doing work by the external force on the electron must always be greater than the rate of radiation of energy by the electron in a case like that under consideration, where the velocity increases continually with the time. Thus

$$f < \left(\frac{3c^3 v_0}{2e^2} \right)^{\frac{1}{2}} F^{\frac{1}{2}}$$

and

$$v_0 < \left(\frac{3c^3 v_0}{2e^2} \right)^{\frac{1}{2}} \int_0^{\infty} F^{\frac{1}{2}} dt.$$

Putting $dx = c dt$, with the path of the corpuscle as the axis of x , and the origin at the point of nearest approach, we have

$$v_0^{\frac{1}{2}} < \left(\frac{3c}{2e^2} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} F^{\frac{1}{2}} dx.$$

Hence,

$$\frac{1}{2} m v_0^2 < \frac{9}{8} \frac{m c^2}{e^4} \left[\left(\int_{-\infty}^{\infty} F^{\frac{1}{2}} dx \right)^4 \right].$$

Now, if p is the distance of nearest approach, the force on the electron due to the corpuscle is *

$$F = \frac{e^2 (1 - \beta^2)^{-\frac{1}{2}} p}{[(1 - \beta^2)^{-1} x^2 + p^2]^{\frac{3}{2}}}.$$

* See, for example, O. W. Richardson, 'The Electron Theory of matter', p. 249.

Hence, putting $(1-\beta^2)^{-\frac{1}{2}}x/p=\alpha$, we readily find

$$\int_{-\infty}^{\infty} F^{\frac{1}{2}} dx = e(1-\beta^2)^{\frac{1}{2}} \int_{-\infty}^{\infty} \frac{d\alpha}{(1+\alpha^2)^{\frac{1}{2}}}$$

and $\frac{1}{2}mv_0^2 < \frac{9}{8}(1-\beta^2)mc^2 \left[\int_{-\infty}^{\infty} \frac{d\alpha}{(1+\alpha^2)^{\frac{1}{2}}} \right]^4,$

or, since the integral is an even function of α ,

$$\frac{1}{2}mv_0^2 < \frac{9}{4}(1-\beta^2)mc^2 \left[\int_0^{\infty} \frac{d\alpha}{(1+\alpha^2)^{\frac{1}{2}}} \right]^4.$$

Putting $\alpha = \tan \theta$, we readily find

$$\frac{1}{2}mv_0^2 < \frac{9}{4}mc^2(1-\beta^2) \left[\int_0^{\frac{\pi}{2}} \frac{d\theta}{\sqrt{\cos \theta}} \right]^4. \quad (2)$$

The integral is known* to be equal to $\sqrt{2} K\left(\frac{1}{\sqrt{2}}\right)$, where K is the elliptic integral

$$K = \int_0^{\frac{\pi}{2}} \frac{d\phi}{\sqrt{1 - \frac{1}{2} \sin^2 \phi}},$$

and is found, from tables, to be equal to 1.854. Thus we find

$$\frac{1}{2}mv_0^2 < 106(1-\beta^2)mc^2. \quad (3)$$

If W is the ionization potential of the atom containing the electron, the energy which must be imparted to the latter to enable it to escape is We , so that ionization will not occur if

$$We \geq 106(1-\beta^2)mc^2,$$

and the highest value of β which will result in ionization is given by

$$1-\beta^2 = \frac{We}{106mc^2}. \quad (4)$$

Taking W as corresponding to 15.5 volts† (0.0517 e.s.u.) for oxygen, we find $1-\beta^2 = 2.98 \times 10^{-7}$, which corresponds to $c-V=45$ metres per second, where V is the velocity of the corpuscle. The conclusion is that a corpuscle moving with a velocity equal to or greater than that corresponding to 45 metres per second less than the velocity of light would be unable to eject an electron from an atom of oxygen, the

* See D. Bierens de Haan, *Tables d'Intégrales Définies*, p. 125.

† See Foote and Mohler, 'The Origin of Spectra,' p. 67.

most easily ionized constituent of the principal gases of the atmosphere. It will, of course, be understood that the value calculated for V merely represents a value which is certainly greater than that at which ionization ceases.

In spite of the very close approximation of the above velocity to that of light, the value 45 metres per second less than the velocity of light happens to be exactly the velocity which Birkeland has found it necessary to assign to solar electrons if the bending which these electrons suffer in the earth's magnetic field is to be consistent with their accounting for the aurora *. Electrons of lower speeds would suffer too large deviations in the field to permit of their accounting for the facts. The diminution of bending resulting from approximation of the velocity to that of light, results not so much from the direct influence of high speed, as from the increase in the mass of the electron which approximation to the velocity of light implies. It is, of course, a fact that, if the present theory were true, it would lead to the conclusion that Birkeland's corpuscles could not ionize at all, so that they could not well account for the aurora; but it is now generally believed that the aurora is not caused by negative electrons, and the comparison with Birkeland's conclusions is only cited to show that, in invoking speeds only 45 metres per second below that of light, one would not be doing anything more drastic than has been already done in other branches of the subject. It may perhaps be worth while pointing out that closeness of approximation to the conditions pertaining to the velocity of light is not well symbolized by closeness of approximation of V to c ; for, as regards the energy of a corpuscle, for example, there is an infinite range from that corresponding to V less than c by 45 metres per second, and $V=c$.

As a special aspect of the above comparison with Birkeland's data, it may be of interest to point out that, if an electron were shot from infinity into our atmosphere—in the equatorial plane, for example,—it would not reach the earth, but would be turned back into space by the earth's magnetic field unless it had a velocity nearer to that of light than the velocity which we have calculated as sufficiently great to insure absence of ionization. Indeed, with this velocity (45 metres per second below the velocity of light) the corpuscle would not succeed in approaching nearer to the earth than about 8 times the earth's radius. (See Appendix, Note 3.)

* See K. Birkeland, 'The Norwegian Aurora Polaris Expedition, 1902-3,' vol. i. Section 2, p. 596.

4. Absorption of the Corpuscles by the Atmosphere.

N. Bohr has worked out a theory for the decrease of velocity of swiftly moving electrified particles in passing through matter *, and has given an expression for the range of such corpuscles. The assumptions of Bohr's theory are such as to render very doubtful the application of the theory to ranges such as those with which we are concerned in the case of the high energy corpuscles under discussion, quite apart from the radiation reactions which we have invoked. If, however, as a matter of general interest, we merely take Bohr's formula and apply it to the present case, we find that for particles with velocity as near to that of light as 45 metres per second, it gives a range certainly more than two kilometres at atmospheric pressure (see Appendix, Note 4). Bearing in mind that the very mechanism by which the corpuscles lose energy on Bohr's theory (the impartation of energy to electrons by which they pass) is denied them, or at any rate greatly curtailed, by the radiation reaction considered in the present paper, we see that there is no obvious difficulty in assuming ranges considerably greater than two kilometres at atmospheric pressure.

It would thus appear that *there is mutual consistency between the phenomena in the statement that if corpuscles should enter our atmosphere from outside, in the equatorial plane, with energies sufficient to enable them to reach the earth's surface in spite of the earth's magnetic field, which would tend to return them to space, they would pass right through our atmosphere with but little absorption, and would fail to ionize the air through which they passed.*

In considering a complete theory of absorption along the lines suggested by the foregoing, it would, of course, be necessary to take into account the energy imparted to the atomic nuclei. The radiation considerations do not operate as forcefully in the case of the nucleus as in that of the electron. However, the amount of energy imparted for a given distance of approach is less in the case of the nucleus than in that of the electron, as may be seen from (7) (Appendix, Note 1) by replacing two of the electronic charges in that formula by nuclear charges, and the electronic mass m_2 by the nuclear mass. In any case, a theory of absorption, even with neglect of radiation considerations, involves complicated considerations which cannot be adequately discussed briefly †, and is not one of the objects of this paper.

* Phil. Mag. ser. 6, vol. xxx. pp. 581-612 (1915).

† N. Bohr, *loc. cit.*

APPENDIX.

NOTE 1. *Concerning the form assumed by Sir J. J. Thomson's theory of ionization when the speed of the corpuscle approximates to that of light.*

Quite apart from all other considerations, it is, of course, not permissible to take the results which have been calculated on the assumption of low velocities and replace the final quantities which occur therein by the expressions which the theory of relativity would assign to those quantities. The proper procedure is to apply the relativity considerations at the beginning of the derivation.

If the corpuscle travels along the axis of x with the origin at the point of nearest approach, and if p is the nearest distance of approach and β the ratio of the velocity of the corpuscle to that of light, the force F on the electron resolved in a direction perpendicular to the x -axis is

$$F = e^2 \frac{(1 - \beta^2)^{-\frac{1}{2}} p}{[(1 - \beta^2)^{-1} x^2 + p^2]^{\frac{3}{2}}} \quad \dots \quad (5)$$

This neglects the effect of variation of the corpuscle's field over the region occupied by the electron itself, a point which is not concerned in our discussion of von Schweidler's conclusion, however.

As explained in Section 3, in the case of corpuscular velocities nearly equal to that of light, it is sufficient to assume that the path of the corpuscle is straight, and to consider only the influence of the above component of the force in calculating the momentum given to the electron. The total momentum given to the electron by the corpuscle of velocity V is,

$$M = \int_0^\infty F dt = \frac{1}{V} \int_{-\infty}^\infty F dx = \frac{e^2}{V} \int_{-\infty}^\infty \frac{(1 - \beta^2)^{-\frac{1}{2}} p dx}{[(1 - \beta^2)^{-1} x^2 + p^2]^{\frac{3}{2}}}.$$

On making the transformation $(1 - \beta^2)^{-\frac{1}{2}} x/p = \tan \theta$, the integral becomes readily evaluated, and we find

$$M = \frac{2e^2}{pV} \quad \dots \quad (6)$$

If m_2 is the mass of the electron in the atom, the velocity attained is M/m_2 , and the kinetic energy gained is

$$Q = \frac{1}{2} m_2 \left(\frac{M}{m_2} \right)^2 = \frac{2e^4}{m_2 V^2 p^2}, \quad \dots \quad (7)$$

showing, as stated in the footnote on p. 308 (Section 2), that the

m in the denominator is really the mass of the electron, and not that of the corpuscle. Following J. J. Thomson's theory, the ionization for one centimetre of the path is proportional to $1/m_2 V^2$.

Equation (7) happens to be exactly the same as the expression resulting from Sir J. J. Thomson's theory for low corpuscular velocities. Thus, the theory in question results in

$$Q = \frac{4T\gamma^2}{m_1 m_2} \frac{1}{\left[1 + \frac{p^2 V^4 \gamma^2}{e^4}\right]}, \quad \dots \quad (8)$$

where T is the kinetic energy and m_1 the mass of the corpuscle, while γ is written for $m_1 m_2 / (m_1 + m_2)$. For all cases of interest, the denominator under the square bracket in (8) is large compared with unity, so that, replacing T by $\frac{1}{2} m_1 V^2$ for low velocities,

$$Q = \frac{2e^4}{m_2 V^2 p^2},$$

which is the same as (7); and, by retaining the subscript 2 in the mass, exhibits this quantity in its true form as the mass of the electron which receives the energy rather than the mass of the corpuscle which imparts the energy.

NOTE 2. *Regarding considerations arising from the finite size of the electron.*

In Section 3 it is implied that the suddenness with which the electron gains such velocity as it acquires increases indefinitely as the speed of the corpuscle approaches that of light, our basis for this assumption being the fact that the field of the corpuscle becomes infinitely contracted towards the equatorial plane of the motion as the velocity of light is approached. The truth of this is only certain when the electron is a point. A finite size for the electron would presumably insure that its gain of velocity was extended over a period at least as great as the time taken by the corpuscle in travelling a distance equal to the electronic diameter, so that increase of the velocity of the corpuscle beyond a certain point would become ineffective in limiting, through further enhancement of the radiation considerations, the energy transmitted to the electron. Moreover, according to strict classical theory, electrons of *finite* radius radiate only finite amounts of energy for infinitely rapid changes from one constant velocity to another, as P. Hertz has shown (*Inaugural-Dissertation*,

Göttingen, 1904) and a corpuscular velocity equal to that of light would not, on strict classical theory, necessarily prevent ionization for electrons of radius 1.8×10^{-13} cm. For infinitesimal electrons the customary expression for radiation is correct.

The origin of the idea of a finite size for the electron is to be found in the fundamental law from which the motion of the electron is usually determined—the law that the electron moves, at each instant, in such a manner that its reaction on itself due to its motion is equal to the force due to the external field integrated over it. In the practical utilization of this law the electron is assumed to be a shell of charge, uniformly distributed over the surface of a sphere when the electron is at rest, and contracted into an ellipsoid when it is in motion, in a manner determined by the requirements of the theory of relativity. When one examines the origin of this law, one cannot avoid being impressed by its artificiality. At the best it seems but a rather crude attempt to go one stage beyond the mere acceptance of a relation between the time derivatives of the motion of the electron and the external force as an empirical fact. It becomes particularly doubtful in a case such as that under discussion, where the field due to the corpuscle varies appreciably over the volume of the electron whose motion is being studied; for it makes no attempt to allow for any dependence of the electronic charge distribution on the variableness of this external field. One who takes this picture of the law of motion as fundamental will, of course, be driven to assume a finite size for the electronic sphere as a result of association of the experimentally measured mass with the quantity which the law assigns to that position. In view of the weaknesses of the law, it would seem not illogical to refuse to be too tightly bound by it if it should turn out convenient to regard the electron as a point in considering its radiation and the action of the external field upon it. On this basis the mass appears simply as a coefficient which relates the acceleration of the electron to the external field; but sacrifice of its complete electrodynamic origin does not prevent our permitting it to vary with velocity in a manner demanded by relativity. In adopting such a procedure, we must be careful that we do not commit a breach of logic by retaining the expression $2e^2 f^2 / 3c^3$ for the rate of radiation of energy by the electron. A consideration of the origin of this expression shows, however, that the assumption concerned is not involved so fundamentally in it as in the matter of the mass; and the expression may still be regarded as retaining

a meaning, even though we discard the electrodynamic origin of mass in the sense ordinarily understood, provided that we still retain the customary expressions for the electromagnetic energy density in the field *. A full discussion of the fine points of this matter would form an article in itself, and would be out of place here. It is fully admitted that a departure from the strict standpoint of classical electrodynamics is made in regarding the electron as a point for the purpose of considering the action of the external field on it; but in making this assumption for the purpose of alleviating the difficulty presented by corpuscular ionization, which matter it is the object of this paper to discuss, we at least replace that very obvious and vital difficulty by one which is concerned with the rather fine points of electrodynamics, and which exists there only when we retain a strict adherence to a form of the law of electronic motion which is itself probably inexact.

NOTE 3. *Concerning the path of a corpuscle entering the atmosphere in the equatorial plane of the earth's magnetic field.*

Imagine an electron projected from infinity along a radius vector directed initially towards the centre of the earth, and lying in the plane of the equator. The magnetic field does no work on the electron, since it acts at all points in a direction perpendicular to the line of flight. As a consequence, the resultant velocity of the electron does not change.

If m is the transverse electromagnetic mass, and ρ the radius of curvature at any point of the path, we have, in electromagnetic units,

$$\frac{mV^2}{\rho} = HeV.$$

Putting $H = M/r^2$, where M is the moment of the earth, we find,

$$\rho = \frac{mVr^2}{eM}.$$

But, if p is the perpendicular distance from the origin, the

* A discussion of some of the points concerned in the relation between the law of electronic motion on the one hand, and electromagnetic mass and energy on the other, will be found in "Fundamentals of Electrodynamics," pp. 33-44, Part I of the National Research Council's report on Electrodynamics of Moving Media.

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origin being on the convex side of the curve, and the radius of curvature being regarded as positive, we have

$$\rho = -r \frac{dr}{dp}.$$

Hence

$$-\frac{dr}{dp} = \frac{mVr^2}{eM}$$

and

$$p = \frac{Me}{mvr}.$$

The constant of integration is zero, since $p=0$ at $r=\infty$.

The smallest value of r is obtained by putting $r=p$, which corresponds to the lowest point of the orbit. Thus, measured from the earth's centre, the lowest altitude attained is

$$\text{Minimum altitude} = \left(\frac{Me}{mV}\right)^{\frac{1}{2}} = \left\{ \frac{Me(1-\beta^2)^{\frac{1}{2}}}{m_0V} \right\}^{\frac{1}{2}},$$

where m_0 is the mass for small velocities. Inserting $1-\beta^2=2.98 \times 10^{-7}$, as given in Section 3, and putting $e/m=1.77 \times 10^7$ e.m.u., $V=c$, and $M=0.9 \times 10^{26}$ e.m.u., we find $p=5.4 \times 10^9$ cm.

NOTE 4. *Concerning conclusions to be drawn from N. Bohr's theory of the "Decrease of Velocity of Swiftly Moving Electrified Particles in passing through Matter"* (Phil. Mag. ser. 6, vol. xxx. pp. 581-612, 1915).

For the range of a corpuscle, Bohr gives in his equation (28) the following expression :

$$R = \frac{m^2 c^4}{2\pi e^4 N \Sigma} \left[(1-\beta^2)^{\frac{1}{2}} + (1-\beta^2)^{-\frac{1}{2}} - 2 \right], \quad (9)$$

where Σ is given by his equation (27) as

$$\Sigma = \sum_1^n \left[\log \frac{k^2 c^2 N n \Delta x}{4\pi \nu^2} - \log \left(\frac{1-\beta^2}{\beta^2} \right) - \beta^2 \right]. \quad (10)$$

In these expressions, N is the number of atoms per c.c., n the number of electrons in an atom, ν a frequency characteristic of the atom and taken by Bohr as given by $(\sum_1^n \log \nu)/n = 38.3$ for air (see p. 597 of his paper). The quantity Δx has a rather complicated meaning for which reference must be made to the original paper. However, it will be seen that its value cannot be comparable

with, or at any rate greater than, the whole range R . If, then, we replace it by R in the equations (9) and (10) above, we shall certainly calculate a value of R which is too small. Moreover, it may be noted that the approximation made by Bohr in treating Σ as a constant during the integration by which he obtains his equation (28) is such as to reduce further the calculated value of R . Of course, the nature of the assumptions in Bohr's theory are such as to render its application to ranges such as we are considering very doubtful. If, however, merely as a matter of general interest we calculate the value of R on the above lines, with Δx replaced by R , and with the value $1 - \beta^2 = 2.98 \times 10^{-7}$ corresponding to the corpuscles we have discussed in Section 3, we find, on using Bohr's data for ν , n , k , etc.,

$$R = 2.2 \times 10^6 \text{ cm.}$$

Ryerson Physical Laboratory,
University of Chicago,
October 10, 1923.

XXVII. *On the Secondary Failure of Thin Tubes of Circular Section subjected to Terminal Couples.* By M. S. AHMED*.

1. IT is well known that cylindrical tubes are liable to secondary failure, if they are sufficiently thin, when subjected to end compression†, as in aircraft construction, or to external pressure as in boiler tubes‡. When thin cylindrical tubes are subjected to terminal couples, their circular sections distort into ovals, and the stresses produced by the change of shape may cause breakdown before the ordinary primary stresses, parallel to the axis, would cause it.

The following investigation is to determine under what conditions the secondary stresses due to deformation of the cross-section into an oval shape exceed the primary stresses found on the ordinary Theory of Pure Bending.

Some possible applications are :—

A monocoque fuselage of an aeroplane which has hitherto been usually built of wood, and might perhaps in the future be made of metal, can possibly be regarded, to a first

* Communicated by Mr. R. V. Southwell, M.A.

† Southwell, "On the General Theory of Elastic Stability," Phil. Trans. Roy. Soc. 1913.

‡ Love, 'Theory of Elasticity,' 3rd edition, Chapter 24 A; Southwell, Phil. Mag. 1913 and 1915.

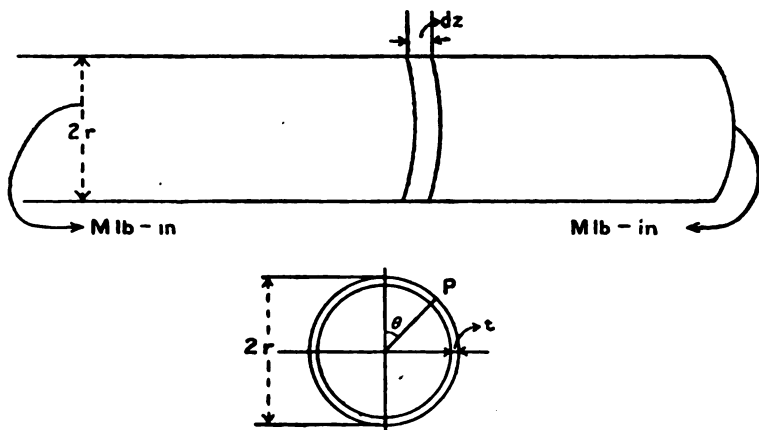
approximation, as a cylinder, bent by wind loads on the tail structure.

A steel factory chimney under wind load is another example.

A somewhat similar stress system possibly arises in a racing eight, or a submarine, under action of the rudder.

The conclusion is that secondary stresses are not likely to be important in steel construction, but are likely to matter in wood ; stiffening rings are then required to compensate.

Fig. 1.



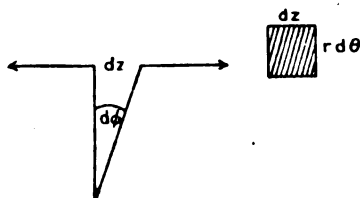
According to the theory of bending, $\frac{f}{y} = \frac{M}{I} = \frac{E}{R}$, where f , y , M , I , &c., have their usual significance (fig. 1),

$$I = \pi r^3 t,$$

$$R = \frac{E \pi r^3 t}{M},$$

at P, f (tensile) $= M \cos \theta / \pi r^2 t$.

Fig. 2.



On an elementary volume $r d\theta dz t$ (fig. 2) there are

Take moments about XX for equilibrium of the portion XXEF,

$$\begin{aligned} M &= M_1 - Q(r)(1 - \sin \theta) + \int_{\theta=\alpha}^{\theta=\pi/2} p \cos \alpha \cdot cr d\alpha \cdot r(\sin \alpha - \sin \theta) \\ &= M_1 - \frac{1}{2} pcr^2 \cos^2 \theta. \end{aligned}$$

From the symmetry of the deformation, it follows that the integrated bending moment from A to F = 0. Hence

$$\int_{\theta=0}^{\theta=\pi/2} di = \int_0^{\pi/2} \frac{M}{EI} r d\theta = \frac{r}{EI} \int_0^{\pi/2} (M_1 - \frac{1}{2} pcr^2 \cos^2 \theta) d\theta,$$

so that

$$M_1 = \frac{1}{4} pcr^2, \quad \text{and} \quad M = -\frac{1}{4} pcr^2 \cos 2\theta.$$

M vanishes when $\theta = 45^\circ$.

Maximum $M = (1/4) pcr^2$ at top or sides, and this produces a maximum stress of amount

$$\frac{3}{2} \frac{pr^2}{t^2} \text{ lb. per square inch.}$$

But

$$p = \frac{Ert}{R^2} = \frac{M^2}{E\pi^2 r^3 t},$$

and therefore maximum stress

$$= \frac{3}{2\pi^2} \frac{M^2}{Er^3 t^3} \text{ lb. per square inch.} \quad . \quad . \quad (1)$$

Compare this with the primary maximum stress

$$f = \frac{M_1}{\pi r^2 t}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For example, take a mild steel tube where

$$t = 0.28 \text{ in.,}$$

$$r = 1 \text{ in.,}$$

$$E = 30 \times 10^6 \text{ lb. per square inch,}$$

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and take maximum stress = 45,000 lb. per square inch, and find M in the two cases :—

From (2) :

$$M_1 = 45,000 \times \frac{22}{7} \times 1 \times .028 = 3970 \text{ lb. inches is the bending moment that would cause failure by primary stress.}$$

From (1) :

$$M_2^2 = 45,000 \times \frac{2\pi^2}{3} \times 30 \times 10^6 (.028)^3$$

or $M_2 = 14,000$ lb. inches is the bending moment that would cause failure by *secondary* stress ; *i.e.*, for aeroplane tubes, ordinary primary stressing is always all right.

As another example, consider a wooden monocoque fuselage, diameter 100 inches and thickness $1/8$ inch :

$$\left. \begin{array}{l} E = 1.3 \times 10^6 \\ f = 5000 \end{array} \right\} \text{ lb. per square inch approximately.}$$

From (2) :

$$\begin{aligned} M_1 &= f\pi r^2 t \\ &= 5000 \times \pi \times 2500 \times 1/8 = 4.9 \times 10^6 \text{ lb. in.} \end{aligned}$$

From (1) :

$$\begin{aligned} M_2^2 &= \frac{2}{3} \times \pi^2 \times f \times E \times r^2 \times t^3 \\ &= 5000 \times \frac{2}{3} \times 1.3 \times 10^6 \times 125,000 \times \frac{1}{512} \end{aligned}$$

or $M_2 = 3.24 \times 10^6$ lb. in.

Hence in this case failure is due mainly to secondary, not primary stresses ; and primary stressing would overestimate the factor of safety by 50 per cent. To compensate the effect considered stiffening rings are generally inserted.

XXVIII. *Heat Dissipation from the Surfaces of Pipes and Cylinders in an Air Current.* By Professor A. H. GIBSON, D.Sc.*

(1) **T**HE following experiments were carried out primarily with a view of obtaining data as to the rate of heat dissipation from tubular metal surfaces adaptable as oil coolers for aircraft. For this purpose a series of tubes of different materials and having different surface coatings were used, made up into spiral coils. The experiments were afterwards extended so as to obtain the relationship between the heat dissipated per unit length of a given pipe when forming part of such a coil, and when exposed normally to the direction of the air current. Also, in order to determine the magnitude of the dimensional effect, a series of experiments were carried out on a straight pipe of considerably larger diameter. A comparison is made between these results and those obtained by Hughes † on a series of copper pipes covering approximately the same range of diameters.

(2) *Apparatus.*—The experiments were carried out in a 6 ft. $\times$ 4 ft. wind tunnel at the Royal Aircraft Establishment, Farnborough. For the tests a number of thin, cold drawn pipes were formed into spiral coils, each 8 inches in diameter and 2 ins. pitch. The length in each case was 12 feet. Each coil was mounted in the wind tunnel with its axis vertical. Hot water was circulated through the coil, the inlet and outlet temperatures and the quantity being carefully measured. In the majority of the tests the temperature of the inlet water was 95°C ., and the mean temperature approximately 90°C . Tests were, however, carried out with inlet temperatures as low as 30°C . in order to obtain the rate of variation of heat dissipation with temperature difference. The air temperature throughout the experiments was approximately 12°C . All these temperatures were accurately measured.

The temperature of the inlet and outlet water was measured by calibrated mercury thermometers, capable of reading to 0.1°C ., fitted into enlargements of the supply and discharge pipes, immediately before and after their connexion to the pipe coil. The connexion between the pipe coil and the supply and discharge pipes was made by rubber junctions. In order to eliminate any end effects and the effect of loss of heat between the thermometers and the

* Communicated by the Author.

† Phil. Mag. vol. xxxi. p. 188 (1916).

experimental pipe, the latter was removed and replaced by a short length (3 ins.) of heavily lagged piping. The difference of readings of the two thermometers at the same mean temperatures and air velocities as in the normal tests was then measured, and this has been deducted from the difference observed in the latter tests.

The flow of water through the pipes ranged from 4 to 7 lb. per minute, and experiments show that over this range the velocity of flow has no appreciable effect on the heat dissipation from the outer surface, so long as the mean temperature remains constant. This can only be the case if the mean temperature of the inner surface is sensibly the same as that of the water, and the assumption has been made in all the tests that this is the case whenever a further increase in the rate of water flow, at a given air speed, is not accompanied by an increase in heat loss from the cooling surface.

Since this is a vital assumption it was decided to check it experimentally, and with this in view two series of tests were carried out on one of the coils. In one series, the heat was supplied by the circulating water. In the other, the heat was supplied by a heavy low-voltage current passing through the coil as a resistance. This was adjusted until the inlet and outlet temperatures of the circulating water were identical, in which case the temperature of the coil is definitely known, as being the same as that of the water. The heat dissipated from the outer surface of the coil is then the equivalent of the electrical energy wasted in the coil, which is known from measurements of the current supplied. The results of these two series of experiments were in very close agreement, the greatest difference not exceeding 2 per cent., and this difference is, in part, to be accounted for by the slight temperature gradient in the pipe wall when the heat is supplied from the circulating water.

Experiments were carried out in still air, in order to obtain the "radiation" loss, which includes the loss also due to natural convection currents, and at wind speeds up to 2000 cm. per sec. (44.5 miles per hour). In each case the wind speed was measured by a calibrated Pitot tube at a point 6 inches up stream from the forward edge of the coil, and opposite its centre. A preliminary exploration of the area covered by the coil showed that the wind speed was sensibly constant over the whole area. Assuming the heat loss to be proportional to the wind speed V raised to some power n , the value of n was deduced from corresponding pairs of experiments at different wind speeds, but at the same mean temperature.

One aluminium pipe was formed into a grid having 7 parallel legs 18 inches long and 3·2 inch pitch, connected by six U bends. In this case the grid was mounted with its plane perpendicular to the direction of air flow, so as to give the cooling effect due to normal impact of the air current.

The details of the pipes are as follow :—

Material.	Form.	Outside diam. cm.	Thickness. cm.
Aluminium	Coil.	1·124	0·142
Aluminium	Grid.	"	"
Copper	Coil.	1·103	·081
Steel	Coil.	0·925	·056
Steel	Straight pipe.	9·520	·254

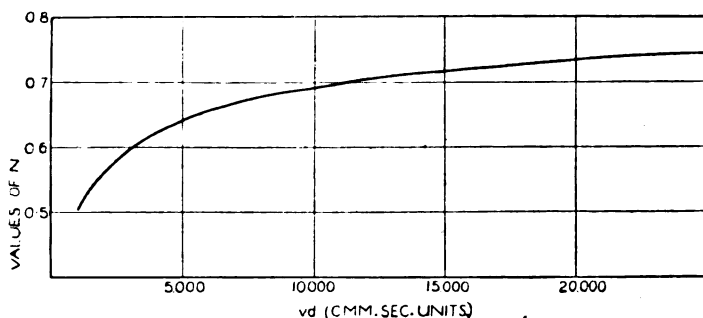
(3) After being tested in the cold drawn state the surfaces of the pipes were treated in various ways, and the pipes were retested. The mean results of a large number of concordant tests are as follow :—

Pipe.	Condition.	Heat loss in calories per sq. cm. per sec. per degree diff. of temp. between water and air at 35° m.p.h. (1568 cm. per sec.)	Heat loss per sq. cm. per degree difference in still air.	Index "n" in $H \propto V^n$.
Aluminium Coil.	Original surface	·00280	·00049	·55
	Sandblasted	·00277	·00053	·55
	Coated with dull black spirit paint	·00293	·00065	·55
	Enamelled black	·00282	·00053	·52
Aluminium Grid.	Original surface	·00330	·00049	·55
Copper Coil	Original surface	·00282	·00053	·50
	Sandblasted	·00284	·00062	·50
	Coated with black spirit paint	·00295	·00065	·70
	Enamelled	·00285	·00056	·50
Steel Coil ...	Original surface	·00327	·00067	·50
	Enamelled black	·00328	·00057	·50
Large Steel Pipe.	Original surface	·00158		·72

In each case the given value of n is the mean over the range of velocities from 800 to 1600 cm. per second. Actually the value of n increases with the velocity and with the diameter of the pipe.

Over a range of velocities from 200 to 2000 cm. per second, its value appears to depend upon the product vd and its approximate values are shown in the curve of fig. 1.

Fig. 1.



(4) *Relative heat dissipation from a pipe coil and from a straight pipe.*—The results of the tests on a pipe coil and on a grid formed of similar pipes mounted normal to the direction of the air flow, show that at speeds between 20 and 45 m.p.h. the heat dissipation is 18 per cent. greater in the latter case.

(5) *Effect of temperature.*—A large number of experiments were carried out to determine the law of variation of heat dissipation with temperature, at a given wind speed. In these the temperature of the hot surface was varied between the limits 30° C. and 90° C., the air temperature being approximately 12° C. Over this range of temperature, the heat loss is proportional, not to the temperature difference θ , but to θ^m , where $m=1.070$ at 800 cm. per sec. and 1.050 at 1600 cm. per sec. This is in general agreement with the results of experiments by Stanton on cylindrical bars* and by Stanton, Booth, and Marshall on copper-finned cylinders†. These results when reduced show $m=1.075$ for an aluminium bar 1.27 cm. diam., 1.065 for a copper bar, at 1100 cm. per sec., and 1.075 for copper fins, over the same temperature range and at about the same mean velocity.

* Advisory Committee for Aeronautics, T. 1010, October 1917.

† Advisory Committee for Aeronautics, T. 929 & I. C. E. 80, April 1917.

(6) *Dimensional effect*.—The principle of dynamical similarity applied to the problem of heat dissipation in an air current, leads to the general result

$$H = \rho l^2 v^3 \phi \left(\frac{\sigma \theta}{v^2}, \frac{k}{\sigma \mu}, \frac{v}{l v} \right), \quad \dots \quad (1)$$

where H is the heat loss per second; ρ the density; σ the specific heat; k the conductivity; μ the viscosity; and v is the kinematic viscosity.

Since for gases $\frac{k}{\sigma \mu}$ is sensibly constant, this becomes

$$H \propto \rho l^2 v^3 \phi \left(\frac{\sigma \theta}{v^2}, \frac{v}{l v} \right), \quad \dots \quad (2)$$

which may be written

$$H \propto \rho l^2 v^3 \phi \left(\frac{k \theta}{\rho l v^3}, \frac{v}{l v} \right). \quad \dots \quad (3)$$

If, as is usually assumed, H is proportional to θ , this becomes

$$H \propto k l \theta \phi \left(\frac{v}{l v} \right), \quad \dots \quad (4)$$

and if, in addition, H is proportional to v^n ,

$$H \propto \frac{k l^{n+1} v^n}{v^n} \cdot \theta. \quad \dots \quad (5)$$

As applied to one of a series of similar pipes, l in this expression refers to any one definite linear dimension, which may be either the length or diameter of the pipe. If, however, the pipes are long, but not of similar length, since the heat loss is proportional to the length, (5) may be written

$$H \propto \frac{k l l^n v^n}{v^n} \cdot \theta, \quad \dots \quad (5')$$

so that the heat loss per unit length of pipe, per degree difference of temperature, will be

$$\frac{H}{l \theta} \propto k \left(\frac{v d}{v} \right)^n,$$

while the heat loss per unit area per degree difference of temperature will, at a given velocity, be proportional to d^{n-1} and, at a given value of $v d$, will be proportional to $1/d$.

If, however, $H \propto \theta^m$, where m is not unity,

$$H \propto \rho l^2 v^3 \phi\left(\frac{\sigma \theta}{v^2}, \frac{\nu}{lv}\right) \\ \propto \rho l^2 v^{3-2m} (\sigma \theta)^m \phi\left(\frac{\nu}{lv}\right). \quad \dots \quad (6)$$

If H is also proportional to v^n ,

$$\phi\left(\frac{\nu}{lv}\right) = \left(\frac{lv}{\nu}\right)^{n-3+2m}$$

and $H \propto \rho l^2 v^n (\sigma \theta)^m \left(\frac{lv}{\nu}\right)^{n-3+2m}, \quad \dots \quad (7)$

or $\frac{H}{l\theta} \propto \frac{\rho v^n \sigma^m \theta^{m-1} d^{n-2+2m}}{\nu^{n-3+2m}}, \quad \dots \quad (8)$

indicating that, at a given velocity and for given temperatures, the heat loss per unit area should be proportional to d^{n-3+2m} and, per unit length, to d^{n-2+2m} , while for a given value of vd , the loss per unit area should be proportional to d^{2m-3} and, per unit length, to d^{2m-2} .

Since, however, ρ , σ , and ν vary with temperature, and therefore with θ for a given initial air temperature, the variation indicated by the θ^m term will include that due to the changing properties of the air. Neglecting the variation in the specific heat as being negligibly small for the range of temperature usual in cooling problems, it is of interest to note what proportion of the total observed variation is due to the change in ρ and in ν or μ .

Over the range of temperatures from 0 to 100° C., $\mu \propto 1 + 0.0026T$ approximately*, where T is the temperature in degrees centigrade; while $\rho \propto \frac{1}{T+273}$. If T° C. is the mean of the temperatures of the inlet air and of the surface it is probably nearly correct to assume that the density and viscosity of the layer of air most directly concerned in the heat dissipation will be that corresponding to this value of T .

The factors ρ and ν are involved in formula (8) in the form $\rho \nu^{3-n-2m}$, or $\rho^{2m+n-2} \cdot \mu^{3-n-2m}$, which is therefore proportional to

$$(T+273)^{2-n-2m} (1 + 0.0026T)^{3-n-2m}.$$

In the author's measurements on the two steel pipes of

* Proc. Roy. Soc. A. vol. lxxx. p. 114 (1908).

diameters 0.925 cm. and 9.52 cm. in two experiments (1) and (2), in which the temperature of the surface was respectively 90°C. and 40° , the air temperature was 10°C. , so that

$$T_1 = \frac{90+10}{2} = 50^{\circ}\text{C.} \quad \text{and} \quad T_2 = 25^{\circ}\text{C.}$$

Giving n the mean value for these pipes, viz. 0.61, and taking $m=1.060$, this makes

$$2-n-2m = -.73,$$

and

$$\frac{(T_1+273)^{-.73} (1+.0026 T_1)^{.27}}{(T_2+273)^{-.73} (1+.0026 T_2)^{.27}} = \frac{1}{1.045}.$$

The corresponding values of the differences of temperatures between metal and air are 80° and 30° , so that

$$\theta_1/\theta_2 = 2.67 \quad \text{and} \quad (\theta_1/\theta_2)^{1.060} = 2.85 = 1.060 \theta_1/\theta_2.$$

From this it appears that of the observed 6.0 per cent. increase in the heat loss h per $^{\circ}\text{C.}$ over this range of temperature, 4.5 per cent. is due to the variation in ρ and μ . Determining by trial the value of m which makes the variation in h proportional to θ^m when the variation in ρ and μ is taken into account, gives $m=1.02$ as compared with the apparent value 1.060 obtained by neglecting this variation.

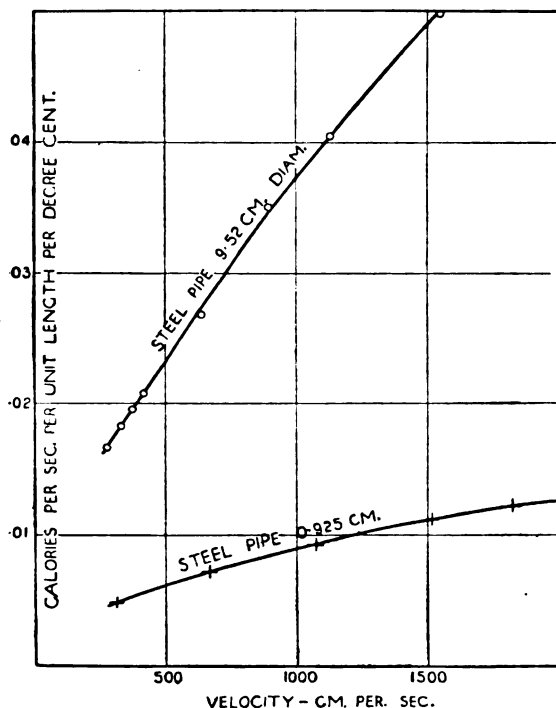
Adopting this value of m in (8), it appears that if the theory of dimensions is to apply to this case of heat transmission the heat loss per unit area per degree at a given velocity and for given temperatures should be proportional to $d^{-.35}$, while for a given value of rd the loss per unit area per degree should be proportional to $d^{-.97}$.

In the two experimental pipes the ratio of the diameters is 10.3. The heat loss per $^{\circ}\text{C.}$ per cm. length of each pipe is shown in fig. 2. At a velocity of 35 m.p.h. (1568 cm. per sec.) the value of h per sq. cm. per degree is .00386 for the small pipe and .00171 for the large one, the ratio being 2.26. The ratio of the two values of $d^{-.35}=2.27$, so that the agreement is almost exact.

Again, at a velocity of 1568 cm. per sec., the value of rd for the small pipe is 1450 cm. sec. For this value of rd , the heat loss per unit area per degree is .000416 calorie per sec. in the large pipe and .00386 calorie in the small pipe, the ratio being 9.3. The ratio of the two values of $d^{2m-3} (=d^{-.96})=9.4$, so that here again the agreement is satisfactory.

(7) *Comparison with results by other observers.*—The results of experiments by Hughes on a series of copper cylinders of diameters .43 cm., .81 cm., 1.93 cm., and

Fig. 2.



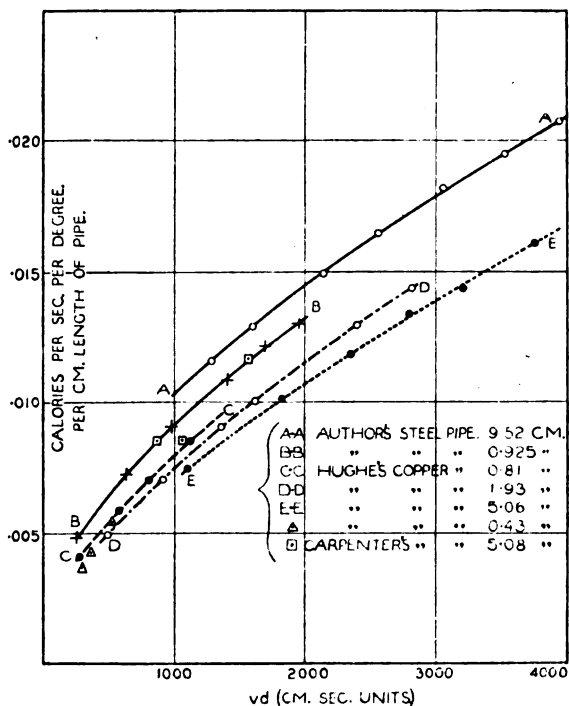
5.06 cm. are indicated by the curves of fig. 3. In these experiments velocities up to 1400 cm. per sec. were used. The copper surface was maintained at a constant temperature of $100^{\circ}\text{C}.$ throughout and the air temperature was apparently $15^{\circ}\text{C}.$ * In the original paper the values of the heat loss are given in calories per unit length of the cylinder, and for comparison the results of the present experiments on the large and small steel pipes have been plotted on the same scale.

The results indicate that for a given value of rd the heat

* The air temperature can only be inferred from the original paper. No definite figures are given except in the radiation tests when it was $15^{\circ}\text{C}.$ It is inferred that it was the same in the convection tests, but to this extent the results are uncertain.

loss per unit length from the author's steel pipes is approximately 20 per cent. greater than the average value obtained by Hughes from the copper pipes having diameters between .43 cm. and 5.06 cm. Since in the author's tests the steel pipes gave a rate of heat loss 7 per cent. greater than the copper pipes (§ 9), this difference, with pipes of the same material, would be reduced to about 12 per cent. It is, moreover, possible that the velocities of air flow given by

Fig. 3.



Hughes are somewhat too high, since the flow was pulsating and a steady reading of the Pitot gauge could only be obtained by using a very viscous oil. In such a case the velocity as calculated from the mean height of the gauge is too high by an amount which depends on the amplitude and periodicity of the fluctuations, but which might readily amount to as much as 12 per cent.

An examination of Hughes's results shows that for a given value of vd the heat loss per degree per unit length of the pipe in some cases increases and in other cases decreases

with an increase in diameter. Thus a pipe 0.43 cm. diam. has a smaller heat dissipation per unit length than one of 0.81 cm. diam., but the latter has a larger heat dissipation than one either 1.93 cm. or 5.06 cm. diameter. Since all these tests were carried out at the same pipe temperature ($100^{\circ}\text{C}.$) and presumably at the same air temperature, no data are available as to the variation of the heat loss with θ . If proportional to θ^m where m is greater than unity, the heat loss per unit length for a given rd should increase with the diameter.

The results of the tests on the largest of Hughes's pipes (15.5 cm. diam.) give values of h much greater than those of the author or of the remaining pipes of his own series. Since the lowest value of rd in the tests on this pipe was 5500 the results are not shown on the curves of fig. 3 or fig. 4. For this value of rd the heat loss per unit length per degree is .034 calorie as compared with .0257 for the author's pipe 9.52 cm. diam., a difference of 30 per cent. There are, however, reasons for thinking that in this particular pipe, which took the form of a short cylinder only 20 cm. long, and in which the end effects would be relatively large, the results given are too high.

Some results are also available of tests by Carpenter * on a pipe 5.08 cm. diam. These are plotted in fig. 3, and are in fairly close agreement with those of the author.

(8) A more testing confirmation of the validity of the dimensional theory is afforded by a comparison with the results obtained by King † on small platinum wires from .003 to .015 cm. diam. at velocities between 17 and 900 cm. per sec. As a result of these experiments, he gives a formula which may be written

$$h/\theta = B \sqrt{rd} \sigma C,$$

where h is the heat loss per cm. length of wire and B and C are sensibly constant. As pointed out by Davis this corresponds to a value of $h=0.66$ calorie per unit length when $rd=1000$ if the temperature of the wire is $100^{\circ}\text{C}.$ and if that of the air is $15^{\circ}\text{C}.$ This makes the heat loss per unit length per degree equal to .00776 calorie per sec. Comparing the largest of the author's pipes (9.52 cm.) with the smallest of King's wires (.003 cm.), the ratio of diameters is 3170, and the ratio of the values of $d^{2m-2}=d^{.04}=1.38$.

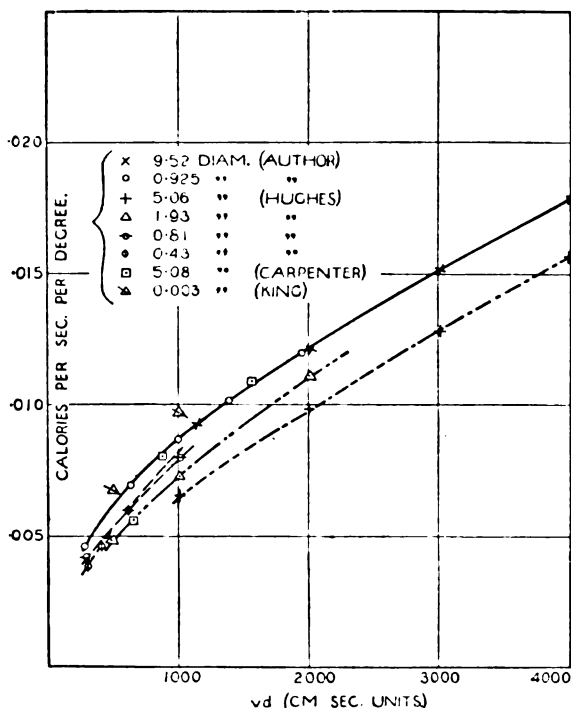
* Quoted by Langmuir, Trans. Am. Electro-Chem. Soc. xxiii. p. 321 (1913).

† Phil. Trans. cxxiv. p. 373 (1914).

According to the dimensional theory the heat loss per unit length from the large pipe when $vd=1000$ should therefore be $\cdot00776 \times 1\cdot38 = \cdot0107$ calorie per sec. per degree. The value computed from the author's experiments is $\cdot0104$, so that over this very large ratio of diameters the agreement is extremely close.

In fig. 4 curves are plotted to represent the heat loss per

Fig. 4.—Heat loss per unit length of a pipe 1 cm. diam. as deduced from tests on pipes and wires having diams. ranging from $\cdot003$ cm. to 9.52 cm.



unit length of a 1 cm. pipe per $^{\circ}\text{C}$. as deduced from the mean results of the tests on each of the above mentioned pipes on the assumption that the heat loss per unit length is proportional to d^{-1} . The author's values for the steel pipes have been reduced by 7 per cent. so as to represent the values for copper pipes.

The results deduced from the experiments of King, Carpenter, and the author agree very closely, while those of the smaller pipes of Hughes are in fair agreement, but are lower.

(9) *Effect of material and roughness of surface on rate of heat dissipation.*—Since the small pipes used in the author's coil experiments are not of identical diameters, the values of the heat loss given in Table I. for the different surfaces are not directly comparable. Correcting these, however, for the small differences in diameter, according to the relationship

$$\frac{H}{ld\theta} \propto d^{n-3+2m},$$

where $m=1.02$, so as to give the loss per unit area of a series of pipes of the same diameter (0.925 cm.) as the steel coil, the following results are obtained:—

TABLE II.

Pipe.	Surface.	Heat loss in calories per sq. cm. per sec. per ° C. difference of temperature between water and air at 35 m.p.h.
Aluminium ...	Original surface	·00305
	Sandblasted	·00302
	Coated with dull black spirit paint	·00319
	Enamelled black	·00309
Copper	Original surface	·00304
	Sandblasted	·00306
	Coated with black paint...	·00318
	Enamelled black	·00307
Steel	Original surface	·00327
	Enamelled black	·00328

From these it appears that the original surface of the steel pipe gives a slightly greater (about 7 per cent.) heat dissipation than that of the aluminium or copper pipes, which are identical. This is apparently due to the fact that the steel pipe was not bright, but had a dull dark finish resulting in a greater loss by radiation than in the other pipes, which were bright though not polished. The effect of the roughening of the surface produced by sandblasting is negligibly small. A coating of black enamel increases the heat transmission of a copper or aluminium pipe by about 1 per cent., but this effect is in all probability due to the fact that the effective diameter is increased by this coating. A coating of dull black spirit paint on a copper or aluminium pipe

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increases the heat dissipation by 4.5 per cent. at this air speed, this effect being largely due to the fact that it increases the radiation loss.

(10) *Conclusions.*—The results of the investigation indicate :—

- (a) At normal air temperatures, and with a hot cylindrical surface at temperatures between 40°C. and 100°C. , the heat loss in a cooling wind is proportional to θ^m , where θ is the difference of temperature and m has a value of 1.02.
- (b) If the changes in density and viscosity of the air with a change in temperature are neglected, the effective value of m is approximately 1.06.
- (c) Taking account of the changes in viscosity and density, the theory of dimensional similarity holds with reasonable accuracy over a range of diameters from .003 cm. to 10.0 cm. and for velocities up to 1500 cm. per sec.
- (d) The value of the index n in $H \propto v^n$ varies with v and with d . For a given value of vd it is approximately constant. It increases from .50 with small pipes at low velocities up to .72 with large pipes at velocities in the neighbourhood of 1800 cm. per sec.
- (e) Except for the greater radiation loss with pipes of dull, dark surfaces, the kind of surface has little effect on the heat loss. The degree of roughening produced by sandblasting has no appreciable effect.
- (f) For copper cooling pipes, the heat loss " h " in calories per cm. of length per degree difference of temperature is given by $h = Kd^{.04}$, where K may be taken as having the following values :—

$vd \text{ (cm. sec. units). } \}$	500	1000	2000	3000	4000	5000	10,000	15,000
$h \dots\dots\dots$	.0062	.0087	.0122	.0152	.0180	.0207	.0320	.0425

For steel pipes, or for pipes painted black, the value of K is to be increased by 5 per cent.

These values apply to wires and to long pipes or cylinders having diameters up to 10 cm. with normal air impact. If formed into a coil with the axis of the coil perpendicular to the direction of air flow, they are to be reduced by 18 per cent.

XXIX. *Recombination of Gaseous Ions, the Chemical Combination of Gases, and Monomolecular Reactions.* By Sir J. J. THOMSON, O.M., F.R.S., Master of Trinity College, Cambridge*.

IF two ions, one at A and the other at B, are left to themselves, they will ultimately separate to an infinite distance if

$$\frac{1}{2} \frac{M_1 M_2}{M_1 + M_2} (V_1^2 + V_2^2 - 2V_1 V_2 \cos \theta) > \frac{\mu}{AB} \quad (1)$$

M_1, M_2 are the masses of A and B respectively, V_1, V_2 their velocities, θ the angle between V_1 and V_2 , μ/r^2 the attraction between A and B when separated by a distance r .

Gaseous ions possess in virtue of thermal agitation a finite amount of energy. We shall suppose that each ion has the mean kinetic energy corresponding to its absolute temperature. If this temperature is θ , then

$$\frac{1}{2} M_1 V_1^2 = \frac{1}{2} M_2 V_2^2 = \frac{3}{2} R\theta = \beta\theta, \quad \text{where } \beta = 2.02 \times 10^{-16}.$$

Substituting these values in (1) and assuming that $\cos \theta$ has its mean value zero, we find that the ions will separate to an infinite distance unless

$$\beta\theta < \frac{\mu}{AB}.$$

Hence, if the ions at A and B possess kinetic energy corresponding to the temperature, they will not recombine if they are at a greater distance apart than $\mu/\beta\theta$. This is on the assumption that they are not subject to any influence other than their mutual attraction. If they are moving through a gas, they may lose some of the kinetic energy which would enable them to separate by one or other of them when they are close together coming into collision with a molecule of the gas.

On the assumption that collision with a molecule restores the kinetic energy of the ion to $\beta\theta$, its value for thermal equilibrium, we see from the preceding investigation that to be effective in preventing separation the collision must occur when the distance between A and B is less than $\mu/\beta\theta$, and that every such collision is effective in producing recombination between A and B.

Hence, to find the number of recombinations per second between the A and B ions, we must describe round the

* Communicated by the Author.

A particles spheres with radii $\mu/\beta\theta$, and find the number of collisions made by the B particles in one second with the molecules of the gas inside these spheres; then describe another set of spheres with the same radius round the B particles, and find the number of collisions per second made by the A particles with the molecules of gas inside these spheres; the sum of the numbers of these two sets of collisions will be the number of recombinations of the A and B ions per second.

If all directions of motion of the A and B particles are equally probable, the number of B particles passing through a sphere round an A particle per second is

$$\pi d^2 \rho' \{U_A^2 + U_B^2\}^{1/2},$$

where $d = \mu/\beta\theta$, ρ' is the number of B particles per unit volume, U_A and U_B the average velocities of the A and B particles respectively.

The number of A particles passing through a sphere round a B particle is

$$\pi d^2 \rho \{U_A^2 + U_B^2\}^{1/2},$$

where ρ is the number of A particles per cubic centimetre.

We proceed to calculate the number of collisions made by the ions in passing through these spheres.

The chance that a B ion will pass through a distance x without making a collision is $e^{-\frac{x}{\lambda'}}$, where λ' is the mean free path of the ion. If the direction of motion of the ion when it enters the sphere makes an angle ψ with the normal, the length of the undisturbed path in the sphere is $2d \cos \psi$. The chance of the angle ψ being between ψ and $\psi + d\psi$ is $\sin \psi d\psi$. Hence the chance of the ion getting through the sphere without making a collision is

$$\begin{aligned} \int_0^{\frac{\pi}{2}} e^{-\frac{2d \cos \psi}{\lambda'}} \cdot \sin \psi d\psi \\ = \frac{\lambda'}{2d} \left(1 - e^{-\frac{2d}{\lambda'}}\right). \end{aligned}$$

The chance that it makes a collision is therefore

$$1 - \frac{\lambda'}{2d} \left(1 - e^{-\frac{2d}{\lambda'}}\right).$$

The chance is, in fact, somewhat greater than this, since the actual path is longer than the undisturbed one.

If, as we have supposed, each collision inside the sphere

results in the combination of the ions, the number of recombinations per second due to the B ions making collisions with the molecules of the gas is

$$\pi d^2 \rho \rho' (U_A^2 + U_B^2)^{1/2} \left(1 - \frac{\lambda'}{2d} \left(1 - \epsilon^{-\frac{2d}{\lambda'}} \right) \right).$$

Similarly, the number of recombinations due to the A ions coming into collision with the molecules of the gas is

$$\pi d^2 \rho \rho' (U_A^2 + U_B^2)^{1/2} \left(1 - \frac{\lambda}{2d} \left(1 - \epsilon^{-\frac{2d}{\lambda}} \right) \right),$$

where λ is the mean free path of an A ion through the gas.

Hence, taking both the A and B collisions into account, we see that the number of recombinations per unit volume per second is equal to

$$\pi d^2 \rho \rho' \{ U_A^2 + U_B^2 \}^{1/2} \left(1 - \frac{\lambda}{2d} \left(1 - \epsilon^{-\frac{2d}{\lambda}} \right) + 1 - \frac{\lambda'}{2d} \left(1 - \epsilon^{-\frac{2d}{\lambda'}} \right) \right).$$

But this number is by definition equal to $\alpha \rho \rho'$ if α is the coefficient of recombination of the ions; hence

$$\alpha = \pi d^2 (U_A^2 + U_B^2)^{1/2} \left(1 - \frac{\lambda}{2d} \left(1 - \epsilon^{-\frac{2d}{\lambda}} \right) + 1 - \frac{\lambda'}{2d} \left(1 - \epsilon^{-\frac{2d}{\lambda'}} \right) \right). \quad (2)$$

Since the attraction between the ions is due to their electrical charges $\mu = e^2$, where e is the charge on an electron, d is given by the equation

$$\frac{e^2}{d} = \beta \theta, \quad \text{where } \beta = 2.02 \times 10^{-16}$$

at 0°C. , $\theta = 273$ and $\beta \theta = 5.5 \times 10^{-14} \text{ erg}$, and since

$$e = 4.8 \times 10^{-10}, \quad d \text{ at } 0^\circ \text{C.} = 4.18 \times 10^{-6} \text{ cm.}$$

The value of d varies inversely as the absolute temperature, but is independent of the pressure of the gas; at 0°C. d is large compared with atomic dimensions, and is comparable with the mean free path of an air molecule at atmospheric pressure.

The value of λ , for an oxygen molecule through oxygen at 0°C. and atmospheric pressure, is $1.02 \times 10^{-5} \text{ cm.}$, which is about 2.5 times the value of d ; so when the pressure is reduced much below 760 mm., d/λ will be a small quantity.

When d/λ is small,

$$1 - \frac{\lambda}{2d} \left(1 - \epsilon^{-\frac{2d}{\lambda}} \right) = \frac{d}{\lambda};$$

so that in this case we get by equation (2)

$$\alpha = 2\pi(U_A^2 + U_B^2)^{1/2} d^3 \left(\frac{1}{\lambda} + \frac{1}{\lambda'} \right). \quad (3)$$

When $2d/\lambda$ is large,

$$1 - \frac{\lambda}{2d} \left(1 - \epsilon^{-\frac{2d}{\lambda}} \right) = 1$$

and

$$\alpha = 2\pi(U_A^2 + U_B^2)^{1/2} d^3. \quad (4)$$

Variation of α with the Pressure.

Since λ and λ' are inversely proportional to the pressure, while d , U_A , and U_B do not alter with it, it follows from equation (3) that at low pressures α is directly proportional to the pressure; while at high pressures, when $2d/\lambda$ is large, equation (4) shows that α is independent of the pressure. Thirkill, who has made measurements of α for several gases through a wide range of pressures (Proc. Roy. Soc. lxxxviii. p. 490), finds that unless the pressure exceeds a certain value, which is a considerable fraction of an atmosphere, α is directly proportional to the pressure; while the experiments of Langevin and McClung show that at pressures higher than one atmosphere the rapid increase of α with the pressure does not continue; α seems to attain a maximum value at a pressure of several atmospheres, and then decreases as the pressure increases. Equation (2) indicates that α would approach asymptotically a constant value as the pressure increases, but would not attain a maximum and then decline.

Numerical Values of α .

If we suppose that the ions in air are charged molecules, and that the average velocity and free path are the same as for an uncharged molecule of oxygen, then at 0°C. and 760 mm.

$$U_B = U_A = 4.25 \times 10^4 \text{ cm./sec.},$$

$$\lambda = \lambda' = 1.02 \times 10^{-5} \text{ cm.}$$

Substituting these values in equation (2), we find

$$\alpha = 1.96 \times 10^{-6} \text{ at } 0^\circ \text{C. and 760 mm.},$$

while the limiting value at very high pressures would be

$$\alpha = 6.5 \times 10^{-6}.$$

The value found for α for air at 0°C. and 760 mm. by Thirkill (Proc. Roy. Soc. lxxxviii. p. 490) is 1.728×10^{-6} ; so that the agreement is quite close. It is closer, indeed, than we should expect, for the free path which we have used in calculating the numerical value of α is that of an uncharged molecule, while the value of λ which occurs in the theoretical value of α is determined by the distance the ion travels through the gas before losing an appreciable amount of energy. The range of action of a charged molecule will be greater than that of an uncharged one: it will therefore be able to communicate its energy to a greater number of molecules; so that the length of path which a charged particle has to travel to lose a definite portion of its energy is shorter than that which would have to be travelled by an uncharged one. This would make the value of λ we have taken too large: on the other hand, if the ions are aggregates of two or more molecules and not single molecules, the values we have taken for U_A will also be too large; so that the two effects will compensate each other to some extent. We shall return to this point as soon as we have considered the effect of temperature on the value of α .

Variation of α with Temperature.

Of the quantities occurring in the expression for α , d is inversely proportional to the absolute temperature θ , while U_A and U_B are proportional to $\theta^{1/2}$; hence we see from (3) and (4) that at low pressures α is proportional to $\theta^{-3}\theta^{1/2}$ or $\theta^{-5/2}$, while at high pressures it is proportional to $\theta^{-2}\theta^{1/2}$ or $\theta^{-3/2}$. In addition to this, there may be, as we shall see, a variation of λ with θ .

The variation of α with temperature has been measured by Erikson (Phil. Mag. xviii. p. 328, 1909, and xxiii. p. 747, 1912), whose experiments were made at constant density, and by Phillips (Proc. Roy. Soc. A, lxxxiii. p. 246, 1910), who worked with constant pressures. Both found a rapid diminution in α as the temperature increased. The relative values of α found by Eriksen for hydrogen at different temperatures are as follows:—

Temp. Abs.	α .
94	6.00
209	.900
296	.45

The Effect of a Charge of Electricity on the Free Path of a Particle.

If M_1, M_2 are the masses of two colliding particles, the transfer of kinetic energy from one to the other produced by a collision is equal to

$$\frac{4M_1M_2}{(M_1 + M_2)^2} T \sin^2 \theta,$$

where 2θ is the angle through which the relative velocity of the particles is turned by the collision, $2T$ is the product of the momentum of the system, the relative velocity of the particles, and the cosine of the angle between these vectors. If either of the particles is at rest, T is thus the kinetic energy of the other; if the masses are equal, T is the difference between the kinetic energies of the two particles.

If one of the particles carries an electric charge and the other is an uncharged molecule, the deflexion 2θ will be due to the attraction exerted by the charge on the molecule. This will be similar in character to that between an electric charge and an uncharged metal sphere, which varies inversely as the fifth power of the distance between the charge and the sphere, provided this distance is considerable in comparison with the radius of the sphere. We shall proceed to calculate the value of θ on the supposition that the law of force between the charged ion and the uncharged molecule is expressed by Ku^5 where $u=1/AB$, AB being the distance between the ion and the molecule. With this law of force the equation of the orbit of the molecule relative to the ion is

$$\frac{d^2u}{d\theta^2} + u = \frac{Ku^3}{h^2},$$

where
$$h^2 = V^2 p^2 \frac{M_1 M_2}{M_1 + M_2},$$

where V is the initial velocity of B relative to A , and p the perpendicular from A on V .

Integrating this equation, we have

$$h^2 \left(\left(\frac{du}{d\theta} \right)^2 + u^2 \right) = \frac{Ku^4}{2} + MV^2,$$

where M is written for $M_1 M_2 / (M_1 + M_2)$,

$$\left(\frac{du}{d\theta} \right)^2 = \frac{Ku^4}{2h^2} - u^2 + \frac{MV^2}{h^2} \dots \dots \dots (5)$$

The apsidal distances are given by equating the right-hand side of this expression to zero; they are the roots of the equation

$$u^4 - \frac{2MV^2 p^2}{K} u^2 + \frac{2MV^2}{K} = 0; \quad \dots \quad (6)$$

for these roots to be real

$$p^4 > 2K/MV^2.$$

For values of p less than this there will be no apsidal distances; the bodies will come together and collide. If the collisions are like direct collisions between elastic spheres, the relative velocity will be reversed by the collision and the bodies will retrace their paths. In this case the relative velocity would be unaltered in magnitude and reversed in direction by the collision, so that θ will be $\pi/2$ and $\sin \theta$ unity.

If b be the value of u at an apse, then by (5)

$$\left(\frac{du}{d\theta}\right)^2 = \frac{K}{2MV^2 p^2} (b^2 - u^2) \left(\frac{2MV^2}{Kb^2} - u^2\right).$$

So that if $u = b \sin \psi$, we have

$$d\theta = \left(\frac{2MV^2 p^2}{K}\right)^{1/2} \frac{d\psi}{\left(\frac{2MV^2}{Kb^2} - \sin^2 \psi\right)^{1/2}}.$$

If $k^2 = \frac{Kb^4}{2MV^2}$, this may be written

$$d\theta = (1 + k^2)^{1/2} \frac{d\psi}{(1 - k^2 \sin^2 \psi)^{1/2}}.$$

The angle 2θ through which the relative velocity of the two particles is twisted is by fig. 1 equal to

$$\begin{aligned} & \pi - 2 \int_0^{\pi} \frac{d\theta}{du} \cdot du \\ &= \pi - 2 \int_0^{\pi/2} (1 + k^2)^{1/2} \frac{d\psi}{(1 - k^2 \sin^2 \psi)^{1/2}} \\ &= \pi - 2 (1 + k^2)^{1/2} F(k), \end{aligned}$$

where

$$F(k) = \int_0^{\pi/2} \frac{d\psi}{(1 - k^2 \sin^2 \psi)^{1/2}}.$$

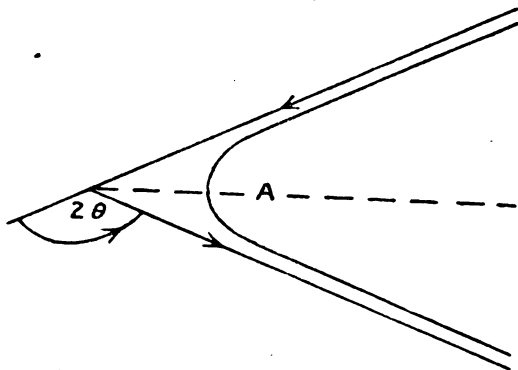
Hence

$$\begin{aligned}\sin \theta &= \sin \left(\frac{\pi}{2} - (1 + k^2)^{1/2} F(k) \right) \\ &= \cos (1 + k^2)^{1/2} F(k).\end{aligned}$$

Thus

$$\frac{4M_1M_2}{(M_1 + M_2)^2} T \sin^2 \theta = \frac{4M_1M_2}{(M_1 + M_2)^2} T \cos^2 \{(1 + k^2)^{1/2} F(k)\}.$$

Fig. 1.



If there are N molecules per cubic centimetre in the gas through which the ion is moving, there will be $N2\pi p \delta p$ collisions per unit length of its path for which p is between p and $p + \delta p$. Hence the loss of energy per cm. due to the collisions between the ion and the molecules is

$$\frac{4M_1M_2}{(M_1 + M_2)^3} T \int \cos^2 \{(1 + k^2)^{1/2} F(k)\} N2\pi p \cdot dp.$$

The lower limit for p , as we have seen, is given by

$$p^4 = 2K/MV^2,$$

and the upper limit is infinity.

Since

$$p^2 = \frac{k^2 + 1}{k} \sqrt{\frac{K}{2MV^2}},$$

$$2\pi p \delta p = \pi \left(1 - \frac{1}{k^2} \right) \sqrt{\frac{K}{2MV^2}} \cdot \delta k,$$

and the limits of k corresponding to those we have prescribed for p are 0 and 1, hence the loss of energy per cm. of path of the ions is

$$\frac{4M_1M_2}{(M_1+M_2)^2} T N \pi \left\{ \frac{K}{2MV^2} \right\}^{1/2} \int_0^1 \left(1 - \frac{1}{k^2} \right) \cos^2 ((1+k^2)^{1/2} F(k)) dk.$$

The definite integral is a numerical constant which, using Legendre's Tables for $F(k)$, I find by quadratures to be about .20. From $p=0$ to $p^2=(2K/MV^2)^{1/2}$, $\sin^2 \theta=1$ and the loss of energy per cm. from these collisions is therefore

$$\frac{4M_1M_2}{(M_1+M_2)^2} T \cdot N \pi \left(\frac{2K}{MV^2} \right)^{1/2}.$$

Thus the total loss of energy due to the collisions is, per unit length of path of the ion,

$$\frac{4M_1M_2}{(M_1+M_2)^2} T \cdot N \pi \cdot 1 \cdot 1 \left(\frac{2K}{MV^2} \right)^{1/2}.$$

This loss of energy is due to the charge on the ion; but even if the ion had not been charged, it would have made collisions which would have produced a transfer of energy. If we suppose that these collisions are like those between elastic spheres; then if s is the sum of the radii of two spheres and p the perpendicular from the centre of one on the velocity of the second sphere relative to the first, then

$$\sin^2 \theta = 1 - \frac{p^2}{s^2}$$

and
$$\int_0^\sigma \sin^2 \theta N 2\pi p dp = \frac{1}{2} N \pi s^2.$$

When we are dealing with the problems on the transference of energy, we may regard $2N\pi s^2 M_1 M_2 / (M_1 + M_2)^2$ as the measure of the reciprocal of the energy free-path of the uncharged molecule, for it measures the number of times per unit length of path that the maximum transfer of energy takes place. When the molecule is charged, the reciprocal of its free path will for the same reason be measured by

$$4M_1M_2 N \pi \times 1 \cdot 1 (2K/MV^2)^{1/2} / (M_1 + M_2)^2$$

Hence, if λ is the energy free-path when the molecule is uncharged, λ' that when it is charged,

$$\lambda' = \frac{\lambda}{2 \cdot 2 (2K/s^2 MV^2)^{1/2}}.$$

Hence, if the free path of the charged molecule is to be much less than that of the uncharged one, $K/2s^4MV^2$ must be considerable.

This quantity is the ratio of $K/4s^4$, the work required to separate an uncharged from a charged molecule with which it is in contact, to $MV^2/2$, the energy possessed by a molecule in virtue of its thermal agitation. We have assumed that there were no collisions for the apsidal orbits, hence $s^4 < 2K/MV^2$ or $2K/s^4MV^2 > 1$).

This result is interesting in connexion with the explanations which have been advanced to account for the smallness of the mobility of the gaseous ions under electrical forces. One theory is that the ions are not simple molecules, but aggregates of a charged molecule with other molecules; another theory is that the small mobility is due to the diminution in the length of the free path caused by the electrical charge on the ion. We shall see, however, later on that the condition that a charged molecule should form aggregates with the other molecules is that K/s^4MV^2 should be considerably greater than unity; but this, as we have just seen, is the condition that there should be a large diminution in the free path of the ion owing to its charge.

Thus the two theories are not alternatives, but inseparable. If complex molecules are formed, there must be an appreciable effect on the free path, and if there is a large effect on the free path, complex molecules must be formed.

We have seen that, when the force between the moving particle and the surrounding molecules varies inversely as the fifth power of the distance, the free path is of the form

$$\lambda' = \frac{\lambda}{1 + \alpha(w/\theta)^{1/2}},$$

where w is the work required to separate the moving particle from contact with a molecule, and θ is the absolute temperature.

If the force between the moving particle and the molecules varied inversely as the third power of the distance, we can show by the same method that the free path would be of the form

$$\lambda' = \frac{\lambda}{1 + \beta w/\theta}.$$

The higher the inverse power of the distance which expresses the law of force between the moving particle and the molecules, the lower will be the power to which (w/θ) occurs in the expression for the modified free path. Since an uncharged molecule exerts forces on another, it follows

from the preceding investigation that the free path in a gas in a normal state must be a function of w/θ , where w is the work required to split up an aggregate of two molecules. The conclusion that the free path of a molecule depended upon the temperature was put forward many years ago by Sutherland, and determinations of the constant C on the assumption that $\lambda \propto 1/(1 + C/\theta)$ have been made by several observers. These values are given in Jeans's 'Dynamical Theory of Gases,' p. 304. Thus for CO_2 , C was shown by Sutherland to be 277. Thus at 0°C ., C/θ would be approximately unity. We may take this as indicating that the work required to separate two molecules of CO_2 is neither a very large multiple nor a small fraction of the energy of thermal agitation at 0°C .; this corresponds to about $1/30$ of a volt.

The value of C for hydrogen is only about 72—about one-quarter of that for CO_2 ; hence we should expect the work required to separate two hydrogen molecules would be about one-quarter of that required to separate two molecules of CO_2 .

Free Path of an Electron.

The case when the moving particle is an electron requires special consideration, since the mass of an electron is exceedingly small compared with that of the molecules with which it collides. We see from the expression on p. 342 that when two colliding bodies have very different masses, the transference of energy by a collision is very small; so that between an electron and a mass as great as that of a molecule there will be very little transference of energy at a collision. Thus, if the gas through which the electrons were moving were hydrogen, the energy transferred at a collision between an electron and a molecule would be only $2/1800$ of that transferred if instead of an electron a hydrogen molecule were moving with the same energy.

It follows from this that the main loss of energy by the electrons is not by collision with the molecules as a whole, but with the individual electrons in the molecule. These electrons have definite periods of vibration, and the amount of energy transferred to them by collision with an electron moving with a definite speed will vary very greatly with the frequency of these vibrations.

The energy the moving electron gives up at a collision with an electron oscillating about a fixed position depends upon the relation between the time of vibration of the fixed electron and the time taken by the moving electron to pass

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over a space equal to the minimum distance between the two electrons. The force between the electrons varies as $1/r^2$; and if c is the minimum distance, v the velocity of the moving electron when in this position, and t the time reckoned from the instant when it passes through the apsidal distance, $r^2 = c^2 + v^2 t^2$ with considerable accuracy. The equation of motion of the fixed electron is

$$m \left(\frac{d^2 x}{dt^2} + n^2 x \right) = \frac{e^2}{c^2 + v^2 t^2},$$

where n is the frequency of the oscillation. The amplitude of the displacement x produced by the collision will be

$$\frac{e^2}{mn} \int \frac{\cos nt}{c^2 + v^2 t^2} dt.$$

We may, since the force only produces a measurable effect when the electrons are near together, take $-\infty$ and $+\infty$ as the limits of integration, since

$$\int_{-\infty}^{+\infty} \frac{\cos nt}{c^2 + v^2 t^2} dt = \frac{\pi}{cv} e^{-\frac{nc}{v}},$$

the displacement produced by the collision is

$$\frac{e^2 \pi}{mn cv} e^{-\frac{nc}{v}},$$

and the energy given to the vibrating electron is

$$\frac{1}{2} \frac{e^4 \pi^2}{m c^2 v^2} e^{-\frac{2nc}{v}}.$$

This expression vanishes when $v=0$, and when $v=\infty$, it has a maximum value for $v=nc$, and is very small for values of v which are either very small or very large in comparison with this critical value.

If T is the time of vibration of the electron, $T=2\pi/n$; so that the critical velocity, *i. e.* the velocity at the apsidal distance for maximum transference of energy, is given by the equation

$$vT = 2\pi c.$$

An electron moving with this velocity would pass over the orbit $2\pi c$ in the time of vibration of the electron which receives the energy. As the apsidal distance c is of the order of the distance of an electron from the central positive charge, the orbit $2\pi c$ would be comparable with an orbit of an electron within the atom, and if an electron describes this orbit in the

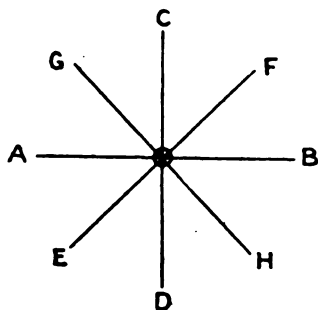
time of vibration of one of the electrons, its energy must be comparable with that required to eject the electron from the molecule—i. e., the maximum transference of energy takes place when the energy of the moving electron is of the same order as the ionizing potential.

Until the critical velocity is reached, the transference of energy increases with the energy of the moving electron; after passing the critical velocity the transference decreases as the velocity of the moving electron increases, and the decrease goes on until the energy of the moving electron approaches that corresponding to another ionizing potential greater than the first, when the transference of energy increases to another maximum and then diminishes again.

The velocity v which occurs in the expression for the transference of energy is the velocity at the apsidal distance, and not V the velocity before the collision occurs. The connexion between V and v will depend upon the distribution of positive charges and electrons in the molecule which contains the vibrating electron, for these, as well as the electron with which it collides, affect the motion of the moving electron before the collision takes place.

Thus suppose the molecule with which the electron collides consists of two positive charges A and B and two electrons

Fig. 2.



C and D at the corners of a square. Then, if the moving electron attains its apsidal distance from C within the regions GOF, EOH, where GH and EF bisect the sides of the square at right angles, the velocity v will be less than the velocity of projection; if it attains the apsidal distance within GOE or HOF, the velocity v will be greater than V ; and if the electron is at its apsidal distance from C when near A or B, v may be very much greater than V .

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We saw from the expression for the transference of energy that but little energy is transferred when $2nc/r$ is large. The forces outside a neutral molecule are very small at distances considerably greater than the radius of the molecule, so that c will be of the order of the radius of a molecule. If V has the value corresponding to thermal agitation at 0°C ., $V = 10^7$, and if $c = 10^{-8}$, then

$$\frac{4\pi c}{T V} = \frac{4\pi \times 10^{-15}}{T}.$$

A value of T equal to $4\pi \times 10^{-15}$ would correspond to a wave-length of about 38,000 Ångström units; as the vibrations of electrons have a much shorter wave-length than this, T must be very much less than $4\pi \times 10^{-15}$; so that, unless the electron gets very much accelerated before the collision, very little energy will be transferred at a collision. Herz found, however, that electrons with this initial velocity lost when passing through hydrogen a few per cent. of their energy at each collision; this is far greater than the energy which would be transferred by a collision between the electron and the molecule if the electrons in the molecule were not thrown in vibration, for this would only be $4 \times \text{mass of electron} / (\text{mass of hydrogen molecule})$ or $1/900$, and also far more than would be transferred by setting the electron in vibration unless the moving electron was greatly accelerated before the collision.

If the electron was so projected that the apse occurred near to either A or B (fig. 2), it would, through the action of the stray field of the molecule, acquire an amount of energy comparable with the ionizing potential, and would therefore lose a considerable amount of energy by the collision. If the initial energy is small compared with the ionizing potential, only a very small fraction of the collisions will result in the apse occurring near A or B; in the other collisions there will be too small an increase of energy to give rise to an appreciable transfer. Thus the average loss at a collision will be but small, but would be sufficient to account for the losses observed by Herz.

When the initial value of the velocity is not far from the critical value, the greatest transference of energy will take place when the apse is in a part of the molecule where the potential differs from that at an infinite distance by a small fraction of the ionizing potential; as this region occupies the greater part of the molecule, a very large fraction of the collisions will result in a transference of the greater part of the energy of the moving molecule to the vibrating one. In this

case the energy free-path of the moving electron will be nearly the same as the geometrical free-path; with smaller velocities the energy free-path will be much longer than the geometrical one.

Rate of Recombination of Electrons and Positive Ions.

In the calculation of the rate of recombination of positive and negative ions given on p. 339, we have assumed that the collision of either a positive or a negative ion with a molecule results in an appreciable loss of kinetic energy by the pair of ions. This will be the case when the masses of the positive and negative ions are not very unequal, for then the increase in the kinetic energy of the pair due to their approach under their attraction will be shared between the ions, so that the energy of each will be increased by a finite amount, which it will lose by collision. When, however, the masses are as different as they are when the carrier of the negative charge is an electron and of the positive charge a positive ion, the increase in the kinetic energy when they approach is practically confined to the body of small mass—the electron,—so that the positive ion has none to lose on collision. In this case the only collisions that give rise to a loss of energy are those of the electrons, and at low pressures the expression for the rate of recombination will be

$$\pi d^3 \{U_+^2 + U_-^2\}^{1/2} \frac{1}{\lambda_-},$$

where λ_- is the mean free path of an electron, and U_+ and U_- the mean velocities of the positive ion and electron respectively. As U_- is large compared with U_+ , the rate of recombination of an electron and a positive ion is approximately $\pi d^3 U_- / \lambda_-$. Since d is the same as for two ions, the rates of recombination for electron and positive ion and for negative and positive ions are as U_- / λ_- is to $2\sqrt{2} U_+ / \lambda_+$, assuming that the U 's and λ 's for the negative ion are the same as for the positive.

The velocity and free path are both greater for the electron than for the positive ion; the value of the ratio of U/λ may depend upon the nature of the gas. Thus for hydrogen, if the positive ion is the molecule, and the electron is in thermal equilibrium with the molecules, the average velocity of the electron is about 60 times that of the molecule. If we take the loss of energy of an electron at a collision as 6 per cent. (see Herz, *Deuts. Phys. Gesell. Verh.* xix. p. 268), it will take some 16 collisions to transfer the energy from the

electron to the molecules, so that the energy free-path will be about 16 times the geometrical one; but the geometrical free-path of the electron is 2.8 times that of a hydrogen molecule, so that the energy free-path of an electron is 44.8 times that of a hydrogen molecule, hence when the free path of the positive ion is the same as that of the molecule

$$U_- = 60 U_+,$$

$$\lambda_- = 44.8 \lambda_+.$$

So that $U_-/\lambda_- = 1.3 U_+/\lambda_+$, and the rate of recombination of electrons and positive ions would be $1.3/2\sqrt{2}$ or .46 times that of negative and positive ions.

The Formation of Complex Ions.

The method we used on p. 339 to calculate the rate of recombination of positive and negative ions can be applied to find the rate of combination of any two attracting systems A and B. We see that the expression (2) will always hold if d is defined to be the distance between the systems when the work required to separate them to an infinite distance starting from d is equal to the energy of a monatomic molecule at the temperature of the system.

There is an attraction between an ion and an uncharged molecule, and if the two combine, the result is a complex ion. We suppose that the attraction between an ion and a molecule follows the same law as that between an electric charge and a metallic sphere. If the distance between the charge and the centre of the sphere is r , the work required to separate them to an infinite distance is $e^2 b^3 / 2r^4$, where b is the radius of the sphere and r is supposed to be considerably greater than b . Hence D , the value of d which occurs in the expression (2), p. 339, is given by

$$\frac{e^2 b^3}{2D^4} = \beta\theta.$$

Thus D varies as $\theta^{-1/4}$, while for the recombination of oppositely charged ions d varies as θ^{-1} .

At 0°C. , $\beta\theta = e^2 / 4.18 \times 10^{-6} \text{ cm.}$, hence

$$2D^4 = b^3 \times 4.18 \times 10^{-6};$$

b will be of atomic dimensions; we shall take it as 10^{-8} , with this value of b ,

$$D = 3.8 \times 10^{-8}.$$

This is only about one-hundredth part of d for two oppositely

charged ions. The rate of combination of the ions with uncharged molecules at low pressures is thus

$$\pi\rho\sigma D^3 (U_i^2 + U_m^2)^{1/2} \left(\frac{1}{\lambda_i} + \frac{1}{\lambda_m} \right),$$

where ρ is the density of the ions, σ that of the uncharged molecules, U_i and U_m the average velocities of the ion and molecule respectively, and λ_i and λ_m their free paths.

The rate of combination between ions of opposite signs is

$$\pi\rho\rho'd^3 (U_i^2 + U_i'^2)^{1/2} \left(\frac{1}{\lambda} + \frac{1}{\lambda'} \right),$$

where ρ' is the density of the ions of opposite sign to those whose density is ρ , and d at 0°C. is 4.18×10^{-6} .

Now, though d is very much greater than D (in the case we are considering d^3 is $10^6 D^3$) yet σ , the density of the uncharged molecules, is in general so much greater than ρ' , the density of the ions, that σD^3 is greater than $\rho' d^3$. At atmospheric pressure σ is 2.7×10^{19} , so that unless ρ' is greater than 2.7×10^{13} , more ions at the beginning will unite with uncharged molecules to form complex ions than with ions of the opposite sign to form neutral systems. It requires very intense ionization to produce 10^{13} ions per c.c. at atmospheric pressure—far more intense than that produced by Röntgen rays of anything like normal intensity, though not more intense than that which frequently occurs in arcs and luminous electrical discharges; and unless the ionization has this high value, an ion will unite with an uncharged molecule to form a complex ion before it ends its career by combining with an ion of opposite sign.

The life of a complex ion may, however, be so short that the proportion of complex to free ions never exceeds a small fraction. Let us suppose that when there are p complex ions per unit volume, kp dissociate per second. Then

$$\frac{dp}{dt} = -kp + \pi\rho\sigma D^3 (U_i^2 + U_m^2)^{1/2} \left(\frac{1}{\lambda_i} + \frac{1}{\lambda_m} \right).$$

The maximum value of p/ρ is thus

$$\pi\sigma D^3 (U_i^2 + U_m^2)^{1/2} \left(\frac{1}{\lambda_i} + \frac{1}{\lambda_m} \right) / k.$$

We proceed to calculate the value of k ; this value will depend upon the mechanism by which the dissociation of the complex ion is effected. We have not nearly as much direct information as is desirable on this point; there is one method, however, which it would seem must be operative,

though whether it is the only one at work is another question. This method is that of collision between complex ions and uncharged molecules. If, as the result of a collision between a complex ion and a molecule moving at high speed, more than a definite amount of energy is communicated to the complex ion, it will dissociate into a simple ion and an uncharged molecule. If a binary system A, B receive at a collision so much energy that

$$\frac{1}{2} \frac{M_A M_B}{M_A + M_B} (V_A^2 + V_B^2 - 2V_A V_B \cos \theta)$$

is greater than the work required to separate A from B, the system will dissociate into A and B. In this expression M_A and M_B are the masses, V_A and V_B the velocities of A and B respectively, and θ the angle between V_A and V_B . The average value of $\cos \theta$ is zero, so that we may write the condition for dissociation as

$$\frac{1}{2} \frac{M_A M_B}{M_A + M_B} (V_A^2 + V_B^2) > Q,$$

where Q is the work required to separate A from B. In the simple case where the complex ion is formed by a positively electrified molecule combined with an uncharged molecule of the same kind, $M_A = M_B$, and the condition for dissociation is

$$\frac{M_A}{4} V_A^2 + \frac{M_B}{4} V_B^2 > Q,$$

or $T > 2Q$ if T is the kinetic energy of the complex ion.

Thus any collision which transfers to the complex ion more than $2Q$ units of kinetic energy will produce dissociation.

We have seen that the energy transferred at a collision between masses M and m is

$$\frac{4Mm}{(M+m)^2} T \sin^2 \theta,$$

where θ depends on the geometry of the collision, *e. g.* the minimum distance between the bodies, as well as upon the law of force between M and m .

The maximum amount of energy which can be transferred at one collision is T , and this is only possible when $M_1 = M_2$ and $\sin^2 \theta = 1$; in this case the bodies in collision exchange energies. When M_1 and M_2 are very different, only a small fraction of the energy is transferred at a collision. It must be remembered that, though when there is a smaller transference of energy at a collision, a molecule will gain less

energy when it collides with a faster molecule, yet it loses less when it collides with a slower ; thus the limiting energy when it attains equilibrium will be independent of the fraction transmitted at each collision. The time taken to attain this state will depend upon the fraction of the energy transferred, and will diminish as the fraction increases.

To dissociate the molecule, $2Q$ units of energy must be gained.

Let us first take the case when the maximum amount is transferred at a collision : then the number of the complex ions dissociated per second is the number of collisions made by the complex ion with the molecules possessing more than $2Q$ units of kinetic energy.

Let u be the velocity of the complex ion; then assuming Maxwell's law for the distribution of velocities the number of molecules it meets per second having velocities between v and $v+dv$ and which are moving so that the perpendicular from the centre of the complex ion on the path of the centre of the molecule is between p and $p+dp$ is

$$\frac{1}{2} \left(\frac{h^3 m^3}{\pi} \right)^{1/2} N 2\pi p dp e^{-hmc^2} v^2 V \cdot dv,$$

where N is the number of molecules per unit volume, V the relative velocity of the complex ion and a molecule of the type we are considering :

$$V^2 = u^2 + v^2 - 2uv \cos \phi, \quad . \quad . \quad . \quad (7)$$

where ϕ is the angle between u and v . When all directions of ϕ are equally probable, the chance that ϕ is between ϕ and $\phi+d\phi$ is $\frac{1}{2} \sin \phi d\phi$. The number of collisions where ϕ is between ϕ and $\phi+d\phi$ is thus

$$\frac{1}{2} \left(\frac{h^3 m^3}{\pi} \right)^{1/2} N \pi p dp e^{-hmc^2} v^2 V dv \sin \phi d\phi,$$

but from (7)

$$V dV = uv \sin \phi d\phi,$$

so that

$$v^2 V \sin \phi d\phi = \frac{vV^2}{u} dV.$$

Integrating with respect to V , and since v must be greater than u , the limits of V are $v+u$, $v-u$, the result is

$$\frac{2}{3} v (u^2 + 3v^2);$$

hence the number of collisions per unit time is got by integrating

$$4 \left(\frac{h^3 m^3}{\pi} \right)^{1/2} N \pi p dp e^{-hmv^2} v^{\frac{2}{3}} (u^2 + 3v^2) dv,$$

where the limits of integration with respect to v are from $\frac{1}{2}mv^2 = 2Q$ to $v = \infty$.

If the maximum transference of energy, i. e. T , occurs at each collision, the integral of this expression with regard to v , from $\frac{1}{2}mv^2 = 2Q$ to $\frac{1}{2}mv^2 = \infty$, will be the number of complex ions dissociated per second. If the energy transferred is only γT , then a single collision will not lead to dissociation unless $\gamma \frac{1}{2}mv^2 = 2Q$. The number of collisions required when v^2 is less than this value will be proportional to $4Q/mv^2$, so that the rate of dissociation will be reduced to the fraction $\gamma mv^2/4Q$ of the value just given. Hence the number of complex ions dissociated in unit time is equal to

$$4 \left(\frac{h^3 m^3}{\pi} \right)^{1/2} N \pi p dp \left[\int e^{-hmv^2} v \cdot \frac{2}{3} (u^2 + 3v^2) \gamma \frac{mv^2}{4Q} dv + \int e^{-hmv^2} v^{\frac{2}{3}} (u^2 + 3v^2) dv \right],$$

where the limits of the first integral are from

$$\frac{1}{2}mv^2 = 2Q \quad \text{to} \quad \gamma \frac{1}{2}mv^2 = 2Q,$$

and for the second from

$$\gamma \frac{1}{2}mv^2 = 2Q \quad \text{to} \quad \infty.$$

In cases where there is appreciable combination, Q will be large in comparison with the energy due to thermal agitation; hence hQ will be large. Making the integrations and retaining only the terms which are most important when hQ is large, we find that the number of times each complex ion is dissociated per second is equal to

$$\begin{aligned} & 4 \left(\frac{hm}{\pi} \right)^{1/2} \cdot N \pi p dp \cdot \gamma \frac{4Q}{m} e^{-4hQ} \\ &= 4 \left(\frac{1}{hm\pi} \right)^{1/2} \cdot N \pi p dp \cdot 4\gamma hQ e^{-4hQ}. \end{aligned}$$

If $\beta\theta$ is the average energy of a molecule at the absolute temperature θ due to the motion of its centre of gravity,

$$\beta\theta = \frac{3}{4h}.$$

and U_m , the average velocity of the molecules at the temperature θ , is equal to $2/(hm\pi)^{1/2}$; hence the number of times each complex ion is dissociated per second is

$$2 U_m N \pi p d p \cdot \gamma \frac{3Q}{\beta \theta} \epsilon^{-\frac{3Q}{\beta \theta}},$$

where

$$\gamma = \frac{4Mm}{(M+m)^2} \sin^2 \theta.$$

If the collisions are like those between elastic spheres,

$$\sin^2 \theta = 1 - \frac{p^2}{s^2},$$

where s is the sum of the radii of the colliding spheres. Substituting this value for γ and integrating from $p=0$ to $p=s$, we find that the number of times a complex ion is dissociated per second

$$= \frac{2Mm}{(M+m)^2} \pi N s^2 \cdot U_m \frac{3Q}{\beta \theta} \epsilon^{-\frac{3Q}{\beta \theta}},$$

where m is the mass of a molecule, and M that of a complex ion. This is the value of k in the equation (see p. 353),

$$\frac{dp}{dt} = -kp + \pi \rho \sigma D^3 (U_i^2 + U_m^2)^{1/2} \left(\frac{1}{\lambda_i} + \frac{1}{\lambda_m} \right) \quad (8)$$

where p is the number of complex ions per unit volume.

Where M is not very different from m , the factor

$$\frac{4Mm}{(M+m)^2} N \pi s^2 U_m$$

in k will be of the same order as the factor

$$(U_i^2 + U_m^2)^{1/2} \left(\frac{1}{\lambda_i} + \frac{1}{\lambda_m} \right)$$

in the second term on the right-hand side of the equation; hence the value of p/ρ when things are in a steady state will be of the order

$$\frac{\pi \sigma D^3}{\frac{3Q}{2\beta \theta} \epsilon^{-\frac{3Q}{\beta \theta}}}.$$

At atmospheric pressure and room temperature, σ the number of molecules per cubic centimetre is 2.7×10^{19} and

(see p. 352) D is about 4×10^{-8} ; hence $\pi\sigma D^3$ is about $\cdot 0054$. Thus, unless the denominator in the expression for p/ρ is very small, the complex ions will only be a small fraction of the free ones.

The following table gives the values of $x e^{-x}$ for various values of x :—

x .	$x e^{-x}$.
4	$\cdot 0732$
5	$\cdot 0336$
6	$\cdot 0148$
7	$\cdot 00637$
8	$\cdot 00266$
9	$\cdot 00110$
10	$\cdot 000453$
12	$7\cdot 4 \times 10^{-5}$

Hence there are about as many complex ions as free ones when $3Q/\beta\theta = 6$, and practically all the ions when $3Q/\beta\theta$ is greater than 12 are complex. Now, measured in volts $\beta\theta$ at 0°C . is about $1/30$ of a volt; hence at this temperature practically all the ions will be complex if β , the work required to separate an ion from the molecule, is as great as $1/7$ of a volt.

These complex ions in virtue of their electric charges will attract uncharged molecules and form ions of a still greater degree of complexity. We see from the preceding investigation that if p_n is the number per unit volume of complex ions which contain n molecules united to the original ion, then

$$\frac{dp_n}{dt} = -k_n p_n + a_n p_{n-1},$$

when k_n and a_n are quantities analogous to the k and $\pi\sigma D^3(U_i^2 + U_m^2)^{\frac{1}{2}} \left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2} \right)$ in equation (2). The value of Q_n , the work required to separate a molecule from a complex ion, will diminish as n increases, and when it falls as low as a small multiple of $1/30$ of a volt, the number of complex ions containing n or more molecules will be very small at 0°C . As long as Q_n is large compared with $\beta\theta$, we should expect the number of ions containing n molecules to increase with the value of n . Thus when complex ions are formed at all they will not be all of the same degree of complexity, but will include ions of different types. These different types will have different mobilities. Experiments on the mobilities of ions have failed to reveal the existence of more than one kind of positive ion, though Langevin's

method, which has been very frequently employed, is peculiarly suited to detect differences of mobilities. Even when a mixture of different gases of widely different densities is ionized by Röntgen rays, the positive ions as determined by their mobilities are all of one type. When we ionize a mixture of, say, hydrogen and methyl iodide, we do not find positive ions of large mobility corresponding to the hydrogen and others of smaller mobility corresponding to the methyl iodide—all the ions seem to have the same mobility. The reason for this will, I think, appear if we consider the times the ions exist in different states.

Life of a Free Ion.

Since the rate of combination of a simple ion with a molecule is (by p. 353)

$$\pi\sigma D^3\{U_i^2 + U_m^2\}^{\frac{1}{2}}\left(\frac{1}{\lambda_i} + \frac{1}{\lambda_m}\right),$$

T the average time the ion exists in the free state is the reciprocal of this quantity, the distance the ion moves in this time is $U_i T$, and the number of free paths contained in this distance is $U_i T/\lambda_i$, or

$$\frac{1}{\pi\sigma D^3} \frac{U_i}{\{U_i^2 + U_m^2\}^{\frac{1}{2}}} \frac{1}{\frac{1}{\lambda_i} + \frac{1}{\lambda_m}}.$$

In the case of the positive ion, U_i and U_m will not be very different, and λ_i will be less than λ_m ; hence number of free paths will not be less than

$$\frac{1}{2\sqrt{2} \cdot \pi\sigma D^3}.$$

Since $\pi\sigma D^3 = .0054$, the number of free paths described by the free ion before it unites with a molecule is about 60 at atmospheric pressure and 0° C. The free path of an ion will in consequence of the charge be somewhat less than that of an uncharged molecule. The free path in air at atmospheric pressure is 10^{-5} cm., so that the distance travelled by the ion in a free state will be somewhat less than 6×10^{-4} cm. As the average velocity of a nitrogen molecule is 4.9×10^4 , the time the ion is free is only about 1.2×10^{-8} second. This time will vary inversely as the square of the pressure, so that at a pressure of .76 mm. of mercury the free ion would exist for 10^{-2} second. As the mobility of a positive ion in air at this pressure is about 1000 cm./sec., the ion could move under an electric

force of 1 volt per cm. through 10 cm. while in a free state. Thus, if the gas between two parallel plates at this distance apart were ionized at this pressure and an electric field of 1 volt per cm. maintained between the plates, the positive ions would be driven against the negative plate before they had united with molecules, so that the mobility determined under these conditions should be that of a simple ion and not that of a complex one. With weaker electric fields some of the ions would become complex before they reached the electrode. Their average mobility would thus be smaller than that under the more intense electric field.

Life of a Free Electron.

We saw (p. 351) that when the mass of one of the two combining particles is very small compared with the other, the rate of combination is

$$\pi\sigma D^3 (U_i^2 + U_m^2)^{\frac{1}{2}} \cdot \frac{1}{\lambda_i},$$

where λ_i is the free path and U_i the velocity of the smaller particle.

This represents the rate of combination of an electron with a molecule. Since U_i is very large compared with U_m , the rate is equal to

$$\pi\sigma D^3 \frac{U_i}{\lambda_i}.$$

T, the average life of an electron in a free state, is the reciprocal of this, $U_i T / \lambda_i$ is the number of free paths described by the electron in the state, so that this number is

$$\frac{1}{\pi\sigma D^3} = \frac{1}{.0054} = 170 \text{ at } 0^\circ \text{ C. and } 760 \text{ mm.}$$

Thus the electron describes about three times as many free paths as the positive ion; but whereas the energy free-path of a positive ion is of the same order as the geometrical free-path (*i. e.* $1/N\pi s^2$) of a molecule, the energy free-path of an electron is very much greater than its geometrical free-path.

The experiments of Herz and Townsend show that when a slowly-moving electron collides with a molecule of oxygen, it only loses a very small percentage of its energy; so that we may take the energy free-path to be of the order of 100 geometrical free-paths, and the path of the electron in a free

state of the order of 170×100 , or 17,000 geometrical free-paths.

Loeb, who has made some very interesting determinations of the life of the free electron in oxygen, finds that it lasts for about 25,000 geometrical free-paths of the electron (Physical Review, xvii. p. 89); this is of the same order of magnitude as that just found.

From Loeb's result, since the velocity of an electron at 0°C. is about 10^7 cm./sec. , we see that the life of a free electron in oxygen at atmospheric pressure is $25,000 \times 4 \times 10^{-5} / 10^7$, or 10^{-7} second. At the pressure of .76 mm. of Hg the time would be $1/10$ of a second. As the mobility of the electron at this pressure is at least 2×10^5 , the electron would under an electric field of a volt per cm. have time to describe 20,000 cm. before uniting with a molecule to form a complex ion. At the pressure of 7.6 mm. it could only describe 20 cm.

We have seen that at atmospheric pressure the life of a free ion is 10^{-8} for the positive ion and 10^{-7} or less for the electron. The time that a positive or negative charge exists, whether as a free or complex ion, before getting neutralized, is in general enormously longer than this. This time is equal to $1/\alpha n$, where α is the coefficient of recombination of the ions and n the number of ions per unit volume. It thus depends upon the intensity of ionization; but as with such intensities of ionization as are usually used in experiments on mobilities it would take at least a second for the ionization to sink to half-value after the ionizing agent has been cut off, the life of a charge must therefore be at least a second at atmospheric pressure, *i. e.* more than a million times that of a free ion.

The preceding calculation of the rate of combination of a free electron with an uncharged molecule is made on the supposition that it requires a finite amount of work to separate the electron from the molecule with which it is supposed to combine. There are, however, some molecules and even some atoms which cannot receive a negative charge. Thus, for example, when there are 8 electrons in the outer layer of an atom, as in neon and argon, the addition of another electron to the outer layer would produce an unstable system which would dissociate spontaneously. Evidence derived from the study of Positive Rays shows that though there are many molecules both of elements and compounds which cannot receive a negative charge, there are others, such as the molecules of hydrogen, carbon, and oxygen, which are able to do so, and it is to these that the preceding investigation applies.

Life of a Complex Ion.

We have calculated the rate at which ions are formed : we now proceed to consider the rate at which they disappear.

If p is number of complex ions and ρ that of free ions per unit volume when things have got into a steady state, then

$$\frac{p}{\rho} = \frac{\text{average life of a complex ion}}{\text{average life of a free ion}};$$

hence by equation (8), p. 357,

$$\begin{aligned} & \text{average life of a complex ion} \\ &= \text{average life of a free ion} \times \frac{\pi\sigma D^3}{\epsilon^{-3Q/\beta\theta}} \cdot \frac{1}{3Q/2\beta\theta}. \end{aligned}$$

At atmospheric pressure $\pi\sigma D^3 = .0054$, and the average life of both an electron and a free positive ion is of the order 10^{-7} second.

The following table gives the value of T , the average life of a complex ion, for different values of $3Q/\beta\theta$:—

$3Q/\beta\theta \dots$	5.	10.	15.	20.
$T \dots\dots$	$.086 \times 10^{-7}$	5.8×10^{-7}	5.8×10^{-5}	7×10^{-3}

Thus, until $3Q/\beta\theta$ approaches 20, the life of an ion in either the free or complex state is only a small fraction of a second. Hence, if the intensity of the ionization is such that the average life of a charge, *i. e.* the time which elapses before it combines with a charge of opposite sign, is as much as one second, the charge during its life will pass backwards and forwards between the free and combined states a large number of times. More generally, if more than one type of complex is possible, the charge will pass in its life through each of these types a large number of times, provided that for any one of these types $3Q/\beta\theta$ is not greater than 20.

In any experiments on ions, such as those on their mobility, if the ions are under observation for a period comparable with one second, the measurements obtained for any property will be the mean of those corresponding to various types of complex ions and not those corresponding to any one particular type. To be able to detect the different types of ions, we should have to employ methods where the times involved were comparable with the lives of the complex ions.

Chemical Combination.

We proceed to consider the application of principles similar to those we have been discussing to the general question of the combination of gases. Before chemical compounds are produced by the combination of two gases A and B, complexes containing the molecules of A and B in close proximity must be formed. We have seen, however, that unless the work required to separate the constituents in a pair of molecules is a considerable multiple of the energy corresponding to thermal agitation, very few such pairs will exist. The work required to separate at temperatures far above that of liquefaction two molecules of a gas will not in general be large compared with the energy of thermal agitation at those temperatures. If we take as the superior limit to the work required to separate two molecules the latent heat of vaporization of one gramme molecule divided by the number of molecules in a gramme molecule, the work required to separate two molecules of hydrogen is expressed by $1/100$ of a volt, that required to separate two molecules of nitrogen by $1/16$ of a volt, while the thermal energy at 0°C. is measured by $1/30$ volt. Thus at this temperature the number of pairs of molecules of either hydrogen or nitrogen would be exceedingly small. Though the molecules of two gases may not be able to form pairs when the gases are pure, they may be able to do so when the gases contain ions. Complex ions will be formed: some of these will contain molecules of A, others molecules of B. If a complex positive ion containing a molecule of A unites with a negative one containing a molecule of B, an addition compound of A and B and the two simple ions will be produced. Again, a complex ion containing a molecule of A combined with a simple ion may form a still more complex one by uniting with a molecule of B, and in this way produce an addition compound of A and B and a simple ion; the life of this compound will be much shorter than that of one formed by two complex ions; on the other hand, the number of free molecules of B will in all probability be much greater than the number of complex ions; so that, though they will not last so long, more of the compounds containing a single ion will be formed. Though we should expect ions to be very efficient promoters of chemical combination, we must remember that in many cases where gases are ionized, *e. g.*, by Röntgen rays, the number of ions is such a minute fraction of the number of molecules that the amount of chemical action cannot be expected to be considerable, though it will be noticed that each ion may lead to

the formation of several molecules of the compound. There are, however, many instances of the effect of ions on chemical combination—such, for example, as the formation of new compounds such as ozone by what is known as the silent electric discharge. Again, Positive Ray Analysis shows that chemical action is very active in the negative glow in a discharge-tube.

A similar effect to that due to ions would occur if, instead of ions, molecules possessing a finite electrical moment, *i. e.* polar molecules, were mixed up with A and B.

These polar molecules exert on neighbouring molecules attractions greater than those exerted by non-polar molecules; so that, if P denotes a polar molecule, complexes (PA) and (PB) may be formed, though the number of pairs (AB) may be insignificant.

The molecules of the aggregates (PA) and (PB) will themselves be polar, and will therefore exert considerable attractions on each other and on simple molecules, the work required to separate them may be a considerable multiple of $\beta\theta$ the energy corresponding to thermal agitation; if this is so, the aggregates PA, B (PA, PB) will be produced in finite quantities. These aggregates are addition compounds of A and B and the polar molecules, so that polar molecules as well as ions may give rise to addition compounds.

The attraction between a polar molecule and a neutral molecule will be less than that between an ion and the molecule if the distance between them is the same; and if the ions were as numerous as the polar molecules, we should expect the former to be more effective in producing chemical combination. But while it is easy to get a large number of polar molecules, *e. g.* by the introduction of a little moisture, it is not, as we have already pointed out, at all easy to get anything like the same number of ions; so that the effect of polar molecules may, as in the experiments of Professor Baker, be more conspicuous than that of ions.

Though ions and polar molecules may in this way lead to the formation of addition compounds, it does not follow that the formation of these compounds would necessarily be followed by that of a true valency compound of A and B. Before two molecules A and B in close proximity can form such compounds, it may be necessary to do work on A and B before the atoms can rearrange themselves in the way necessary for the formation of such a compound. Thus, for example, though in the combination of H_2 and Cl_2 , a great deal of work is given out when $2HCl$ has once been formed, yet before the rearrangement of the atoms necessary

for this can occur, work may have to be supplied to split up the H_2 and Cl_2 molecules : a catalyst which will either wholly supply this work or diminish the amount materially may be required. It is important to notice that ions and polar molecules, besides promoting the formation of addition compounds, may themselves act as catalysts. Thus, for example, the presence of an electron or the negative end of a polar molecule near the positive end of the system $A-A$ will diminish the work required to move A_+ from A_- , promoting the rearrangement of the atoms in the A molecule and thus acting as a catalyst.

Thus the presence of either charged ions or polar molecules does two things, each of which promotes chemical combination :—

- (1) It promotes the formation of addition compounds.
- (2) The ions and polar molecules act like a catalyst in helping the rearrangement of the atoms necessary to convert the addition compound into the final chemical one.

To form some estimate of the rate at which chemical combination might be expected to occur under the influence of ions and polar molecules, we may proceed as follows :—

Let us take the case when, as in the union of hydrochloric acid gas and ammonia, one molecule of a gas A unites with one of a gas B to form a molecule of the compound.

Let (A) , (B) be the number of A and B molecules respectively per unit volume ;

(p) the number of ions or polar molecules per unit volume ;

(pA) the number of complexes per unit volume of an ion or polar molecule with a molecule of A .

The addition compounds of A and B due to the ions may be of the type $\{(pA)(pB)\}$ or $\{(p \cdot A)(B)\}$.

We shall suppose that addition compounds pass immediately into chemical compounds, and that these when once formed do not decompose ; so that the rate of formation of these additive compounds is the same as that of the chemical one.

Since the addition compound is supposed not to dissociate,

$$\frac{d}{dt}(pA \cdot pB) = a(pA)(pB) \dots (9)$$

and

$$\frac{d}{dt}(pA, B) = a'(pA)(B), \dots (10)$$

where a and a' are the coefficients of combination of pA and pB and of pA and B respectively.

Now a and a' are of the form (see p. 339)

$$\pi d^3 \cdot (u^2 + u_1^2)^{1/2} \left(\frac{1}{\lambda} + \frac{1}{\lambda'} \right).$$

This in a gas at atmospheric pressures and temperatures is of the order

$$\pi d^3 \times 10^9.$$

d is the distance between the two combining molecules when the work required to separate them is equal to the energy of thermal agitation; if one of these molecules has a positive and the other a negative charge, as in the addition compound formed by complex ions, then (see p. 339)

$$d = 4.18 \times 10^{-6} \quad \text{and} \quad \pi d^3 \times 10^9 = 2.3 \times 10^{-7}.$$

If all the ions are complex, and if there are as many A molecules as B and the free ions distribute themselves equally between A and B, then

$$(pA)_+ = (pA)_- = (pB)_+ = (pB)_- = \frac{1}{4}p$$

and (9) becomes

$$\frac{d}{dt}(pA \cdot pB) = \frac{a}{16} p^2 = \frac{2.3}{16} \times 10^{-7} p^2.$$

If there is one ion for every million molecules, then at atmospheric pressure and 0°C .

$$p = 2.7 \times 10^{13},$$

$$\frac{d}{dt}(pA \cdot pB) = 1.03 \times 10^{19}.$$

Now there are only 1.35×10^{19} molecules of A and B per unit volume, so that with this rate combination would be complete in a time comparable with one second. We could not, however, get ionization approaching this in intensity except in intense electrical discharges through gases. For ionization by Röntgen rays one ion per 10^{10} molecules would be a high estimate, and in this case it would take a time comparable with 10^8 second, or more than three years, for the combination to be complete.

When the addition compound is $(pA \cdot B)$, the value of d is 4×10^{-8} (see p. 352) and $\pi d^3 = 2 \times 10^{-22}$, hence a' is of the order 2×10^{-13} ; and if all the ions are complex $(pA) = p/4$; and

$$\frac{d}{dt}(pA \cdot B) = .5 \times 10^{-13} p(B).$$

If there is one ion per million molecules and the gas is at atmospheric pressure,

$$p = 2.7 \times 10^{13},$$

$$(B) = \frac{1}{2} \times 2.07 \times 10^{19};$$

so that

$$\frac{d}{dt}(pA \cdot B) = 1.4 \times 10^{19},$$

and the combination would be complete in less than one second; if there was one ion per 10^{10} molecules, the combination would be complete in about 3 hours.

Let us now pass on to the case when instead of ions we have polar molecules. If m is the electrostatic moment of a molecule, the work required to separate two such molecules separated by a distance r is m^2/r^3 , or if $m = e \times 10^{-8}$, $e^2 \times 10^{-16}/r^3$; hence d will be given by

$$\begin{aligned} \frac{e^2 \times 10^{-16}}{d^3} &= \beta\theta, \\ &= \frac{e^2}{4.18 \times 10^{-8}} \text{ at } 0^\circ \text{ C.} \end{aligned}$$

So that

$$d^3 = 4.18 \times 10^{-22}$$

$$\text{and } \pi d^3 \times 10^9 = 1.3 \times 10^{-12}.$$

Thus

$$\frac{d}{dt}(pA \cdot pB) = 1.3 \times 10^{-12} \times (pA)(pB).$$

We have to remember that in general a large proportion of polar molecules are free and uncombined. Let us suppose that only one per cent. are combined, and that those which are combined are distributed equally between A and B, so that $(pA) = p/200 = (pB)$; then

$$\frac{d}{dt}(pA \cdot pB) = \frac{1.3}{4} \times 10^{-16} p^2.$$

If there is one polar molecule to 10^4 of the others, $p = 2.7 \times 10^{15}$, so that

$$\frac{d}{dt}(pA \cdot pB) = 2.37 \times 10^{14},$$

a rate which would make the combination complete in a little over a day.

When the addition compounds are of the form (pA, B) , since the work required to separate an electric doublet whose

moment is m from an uncharged molecule of radius b is of the order

$$\left(\frac{m}{r^3}\right)^2 \frac{4}{3}\pi b^3,$$

if d is the distance when this work is equal to the thermal energy at 0°C. , then

$$\left(\frac{m}{d^3}\right)^2 \frac{4}{3}\pi b^3 = \beta\theta = \frac{e^2}{4.18 \times 10^{-6}}.$$

m will be of the order $e \times 10^{-8}$ and b of the order 10^{-8} ; so that

$$d^6 = 4.2 \times 4.18 \times 10^{-46}$$

$$\text{or} \quad \pi d^3 = 1.26 \times 10^{-22}.$$

Hence

$$\frac{d}{dt} (pA \cdot B) = 1.26 \times 10^{-13} \times (pA)B.$$

If one in a hundred of the polar molecules are combined with the other molecules, $(pA) = p/200$. Hence at atmospheric pressure, if there is one polar molecule for 10^4 combining molecules,

$$(pA) = 1.35 \times 10^{13}, \quad B = 1.35 \times 10^{19},$$

$$\text{and} \quad \frac{d}{dt} (pA \cdot B) = 2.3 \times 10^{19};$$

so that the combination would be complete in about one second. If there were only one polar molecule in a million of the others, the combination would be complete in about a minute. These numbers illustrate the enormous effect of traces of polar molecules on chemical combination.

Velocity of Monomolecular Reactions.

The investigation we gave for the rate of dissociation of a complex ion would apply to the dissociation of any gaseous molecule if this is due to molecular impacts. In this case, if

$$\frac{dP}{dt} = -kP,$$

k is of the form

$$\frac{Q}{k\theta} \frac{U_m}{\lambda} e^{-\frac{Q}{R\theta}}, \quad \dots \dots \dots (11)$$

where θ is the absolute temperature, Q the energy required

to dissociate the molecule, U_m the mean velocity of the molecules at the temperature θ , and λ the mean free path of the molecule ; U_m/λ is the reciprocal of the time of relaxation of the gas, and is proportional to the pressure.

The subject of monomolecular reactions has excited a good deal of attention, and expressions for the rate have been published by Dushman (Journal of the Franklin Institute, clxxxix. p. 515), Trautz (*Zeitsch. für Physik*, xi. p. 113, 1920), Rice (Phil. Mag. xlv. p. 312), and McKeown (Phil. Mag. xlv. p. 321). A general account of what has been done in this subject, together with a bibliography, is given by Harned (Proc. Franklin Inst., Aug. 1923). None of these authors, however, attributes the dissociation to molecular impacts ; in fact, the laws of dissociation have been supposed to rule this explanation out of court. I pointed out in my 'Applications of Dynamics to Physics and Chemistry,' p. 201 (1888), a difficulty which is met with by supposing that the decomposition of gaseous molecules is due to collision. This may be put as follows :—If m is the number of undissociated molecules, k_1 the rate of dissociation, n the number of atoms, k_2n^2 their rate of combination, then when things are in a steady state

$$k_1m = k_2n^2.$$

It follows from thermodynamical principles that m/n^2 is not affected by the presence of a neutral gas ; but if the dissociation is due to molecular impacts, k_1 will be increased by the introduction of an inert gas, for the number of impacts will be increased, and *if the presence of the inert gas does not increase the number of combinations, n^2/m would be increased, which is not the case.* The argument is sound if the statement in italics is true. We have seen, however, in the discussion of the rate of recombination of gaseous ions that this rate is affected by the pressure of the gas, and that when this pressure is not too high the rate is directly proportional to the pressure, and this result is confirmed by Thirkill's experiments on the rate of recombination of ions. This result ought to apply, if the theory is correct, to all cases of gaseous recombinations which occur in the body of the gas and not on the sides of the vessel in which the gas is contained.

The rate of recombination of dissociated atoms would be increased by the presence of a neutral gas ; thus k_2 will be increased, and if n^2/m is to remain constant, k_1 must increase too, as it would do if the dissociation were due to collisions. Thus the laws of dissociation support the view that the dissociation is due to collisions.

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Professor Perrin (*Ann. de Chimie et de Physique*, xi. p. 5) quotes the absence of appreciable electrical conductivity in many cases of chemical combination as an objection to the view that ionization is due to collisions, for we know from experiments on Positive Rays that rapidly-moving molecules ionize by collision the gas through which they are moving. It is known, however, that this ionization does not take place to any appreciable extent unless the energy of the moving molecules exceeds a critical value which is very high (the lowest value yet found by experiment corresponds to 300 volts, which is far in excess of the energy required to dissociate a molecule into neutral atoms).

Experiments have been made to test the truth of various expressions for the rate of monomolecular reactions: the dissociation of phosphine (Trautz, *Zeitschrift Anorg. Chem.* cvi. p. 95, 1919), H_2 , I_2 , Br_2 , Cl_2 (Dushman, *loc. cit.*), have been used for this purpose. It must, however, be noted that when $Q/R\theta$ is large, as it is for all these gases, the factor $e^{-Q/R\theta}$ which occurs in all the expressions for k so dominates its value that a small percentage change in the value assigned to Q would more than cover the differences in the other factor occurring in the value of k given by different writers. A more searching test would be to find the values of k at a given temperature for I_2 or N_2O_4 when these gases are mixed with inert gases at different pressures, care being taken that the effects due to the walls of the vessel are eliminated. Experiments with this object are in progress at the Cavendish Laboratory.

From equation (11) we have, since U_m varies as $\theta^{\frac{1}{2}}$,

$$\frac{d \log k}{d \log \theta} = \frac{Q}{R\theta} - \frac{1}{2}.$$

Since $Q/R\theta$ is large, this is a close approximation to the empirical formula given by Arrhenius:

$$\frac{d \log k}{d \log \theta} = \frac{Q}{R\theta}.$$

When the substance concerned in the monomolecular reaction is a solid and not a gas—as, for example, in the problem of the rate of sublimation of a solid—we cannot suppose that impacts between the molecules are the cause of the transference of large quantities of energy to the molecules which are liberated from the solid. We can, however, on lines analogous to those used for gaseous reactions, obtain an expression for k .

The molecules of a solid are arranged along lattices, and if one of the molecules is struck, a pulse will spread through the system, displacing the molecules as it passes over them. Thus we may regard the solid as the seat of a very large number of pulses which are continually displacing the molecules from their equilibrium positions. These pulses are so numerous that each molecule is affected by a very large number of them simultaneously, and the phases of the different pulses are arbitrarily distributed. Thus the effect of these pulses on the displacement of a molecule will be obtained by the same rule as that which gives the resultant of a large number of displacements of arbitrary phase. This problem was solved by Lord Rayleigh ('Theory of Sound,' 2nd edit. vol. i. p. 42), who showed that the probability of the amplitude being between r and $r + dr$ was in the three-dimensional problem

$$3 \sqrt{\frac{6}{\pi n^3}} \epsilon^{-r^2/\frac{2}{3}n} r^2 dr, \quad (12)$$

where n is the mean value of r^2 .

The energy of the molecule is proportional to r^2 , and if we assume that the mean energy of the molecules is as in a gas proportional to the absolute temperature and denote as in a gas $2/3$ of this energy by $R\theta$, the probability of a molecule having energy between T and $T + dT$ is, from (12),

$$2 \sqrt{\frac{1}{\pi(R\theta)^3}} \epsilon^{-T/R\theta} \sqrt{T} \cdot dT.$$

The probability of a molecule having energy greater than Q is therefore

$$2 \sqrt{\frac{1}{\pi(R\theta)^3}} \int_Q^\infty \epsilon^{-T/R\theta} \sqrt{T} \cdot dT.$$

An approximate value of the integral when $Q/R\theta$ is large is

$$R\theta \epsilon^{-Q/R\theta} \sqrt{Q};$$

so that the probability of the molecule having energy greater than Q is approximately

$$\frac{2}{\sqrt{\pi}} \epsilon^{-Q/R\theta} \left(\frac{Q}{R\theta}\right)^{\frac{1}{2}}. \quad (13)$$

It should be mentioned that this result does not depend upon all the impulses having the same intensity; it holds when the pulses have different intensities, provided there

are always enough of each type acting on a molecule to justify the employment of statistical methods.

If Q is the work required to separate the molecule from the solid, (13) will give the probability of a molecule at the surface being in a condition to escape from it. To find the rate at which they escape, we must find the rate at which the supply of these active molecules is renewed.

It is evident that after a time equal to that which a pulse requires to travel over a distance equal to its thickness, the distribution of resultant intensities will change entirely: the molecules which at first were at places where the superposition of the pulses was such as to give a large resultant will no longer do so; on the other hand, some molecules which are at places where the resultant amplitude had previously been small will now find themselves vibrating with a larger amplitude. Thus T , the time taken by a pulse to pass over a distance equal to its thickness, is the average time taken by the molecules which are in a particular state with respect to energy to change into another state. Thus, if P is the number of molecules which have energy greater than Q , P/T will be the number which pass out of this state per second, and this when things have settled down into a steady condition will be the number which in one second acquire energy greater than Q . Hence, if N be the number of molecules, the number that pass per second into a state where the energy is greater than Q is

$$\frac{1}{T} \frac{2N}{\sqrt{\pi}} \left(\frac{Q}{R\theta} \right)^{\frac{1}{2}} e^{-Q/R\theta}.$$

So that

$$k = \frac{1}{T} \frac{2}{\sqrt{\pi}} \left(\frac{Q}{R\theta} \right)^{\frac{1}{2}} e^{-Q/R\theta}.$$

To determine the value of T , we notice that pulses of the kind we are considering will not only excite the motion of the molecules, but will also start pulses of radiation of the same duration. All bodies give out a continuous spectrum in which λ_m , the wave-length where the energy is a maximum, is by Wien's law inversely proportional to the absolute temperature and at 0°C. is about 10^{-3} cm. If we regard this light radiation as made up of pulses, λ_m will be a measure of the average thickness of the pulse and λ_m/c , if c is the velocity of light, will be the duration of the effect which gave rise to the pulse. If we suppose that the radiation arises from the pulses of molecular displacement, this will be equal to T , so that $T = \lambda_m/c$.

Thus k , the rate of monomolecular reaction in a solid, will be given by the equation

$$k = \frac{c}{\lambda_m} \frac{2}{\sqrt{\pi}} \left(\frac{Q}{R\theta} \right)^{\frac{1}{2}} e^{-Q/R\theta}.$$

Since λ_m is inversely proportional to θ ,

$$\frac{d \log K}{d \log \theta} = \frac{Q}{R\theta} + \frac{1}{2}.$$

The value of k for a solid bears to that for a gas, Q and θ being the same for the gas and solid, the ratio of

$$\frac{c}{\lambda_m} \text{ to } \left(\frac{Q}{R\theta} \right)^{\frac{1}{2}} \frac{U_m}{\lambda},$$

where λ is the mean free path of a molecule and not a wave-length.

Since at 0°C. $c/\lambda_m = 3 \times 10^{13}$ and U_m/λ is of the order 10^9 at 760 mm., we see that unless $Q/R\theta$ is exceptionally large, or the pressure of the gas very high, the value of k for a solid will be considerably greater than that for a gas.

Influence of the Walls of the Vessel on Gaseous Reactions.

The expression we have deduced for the rate of gaseous reactions is founded on the assumption that these take place in the body of the gas. Van't Hoff long ago showed that the walls of the vessel in which the gas is contained often exert great influence on the velocity of the reaction. A very striking instance of this effect is given by Bodenstein (*Zeitsch. f. Physik. Chem.* xxix. p. 689), who found that the combination of hydrogen and oxygen at the temperature of 600° occurred entirely at the surface of the vessel in which the gases were contained.

The conditions for chemical combination at a surface are quite different from those for the body of the gas. It would seem that the first stage towards the union of two atoms or molecules A, B would be for these to form molecular compounds with the molecules at the surface, and give rise to a surface layer of molecules which may be denoted by SA, SB. SA and SB then form addition compounds, from which AB is deposited on the surface; it may subsequently evaporate and find its way to the body of the gas.

With regard to the formation of SA, SB, the molecules of the solid are so close together that the opportunities of getting rid of superfluous energy are great enough to make almost

every molecule which strikes against the surface form a molecule compound with it if it is clean.

Thus the rate of formation of these molecular compounds will not be affected by the pressure of the inert gas, nor will the rate of formation of the addition compounds formed from the systems SA, SB condensed on the surface. Again, the rate at which AB evaporates from the surface will be expressed by a formula similar to that for the evaporation of a solid. Thus in this case the only way an inert gas can affect the rate of the chemical reaction is by forming a layer on the surface of the solid and protecting it from the action of A and B. This would retard the combination, while for reactions in the body of the gas the effect of the inert gas would be acceleration. Thus it is necessary in studying gaseous reactions to separate the part occurring on the surface from that occurring in the body of the gas.

Another view of the origin of monomolecular reactions is that they are due to radiation. The energy in the black body radiation at θ with a frequency between ν and $\nu + d\nu$ is proportional to

$$\nu^2 \frac{h\nu/R\theta}{e^{h\nu/R\theta} - 1} \cdot d\nu,$$

or, if $h\nu/R\theta$ is large, to

$$\nu^2 \cdot h\nu/R\theta e^{-h\nu/R\theta} d\nu.$$

If the monomolecular reaction was due to radiation within a small range of frequency—fixed for each substance—and proportional to the energy of this kind of radiation, the expression for the rate would contain the factor $e^{-h\nu/R\theta}$, and if ν were determined by the quantum relation

$$Q = h\nu,$$

this factor would become $e^{-Q/R\theta}$, which is the law indicated by experiment. This view is, however, open to very serious objection, for, as Professor Lindemann has pointed out, the intensity of the radiation may by artificial illumination be increased many thousandfold without any commensurate increase in the rate of the reaction. It is not, as we have seen, necessary to have recourse to radiation to get the factor $e^{-Q/R\theta}$ in the expression for the rate of radiation.

The expressions for the velocity of chemical reactions illustrate and explain the enormous influence of water-vapour, of surface effects, of impurities, of catalysts generally

upon the progress of chemical combination. For these expressions for the rate of the reaction contain as a factor $\epsilon^{-Q/R\theta}$, where Q is the work required per molecule to bring the substance from the initial to the final state. When Q is large compared with $R\theta$, this factor is exceedingly small.

If the circumstances are such as to admit of the transition from the initial to the final stage taking place in two stages instead of one, the velocity of the reaction may be increased enormously. To take an example: suppose the complete reaction involved a value of Q represented by two volts, the factor $\epsilon^{-Q/R\theta}$ would at 0°C. be equal to ϵ^{-60} ; if, however, the change took place in two stages, the factor $\epsilon^{-Q/R\theta}$ for each stage would be ϵ^{-30} (supposing the energy changes to be equally divided between the two stages). Now ϵ^{-30} is about 10^{13} times ϵ^{-60} , so that the velocity of the reaction would be increased more than a billion times by dividing it into two stages.

The effect of polar molecules, of free surfaces, of impurities, &c. is to provide opportunities for the formation of phases intermediate between the initial and final one, such that the transference from one phase to the next requires the expenditure of much less energy than that from the initial to the final one. These small energy changes go on with so much greater rapidity than the large one, that though several are required to complete the change from the initial to the final state, this is overbalanced to an overwhelming extent by the much greater rapidity of the individual changes.

To take an example: if the reaction we are considering is the dissociation of AB into A and B . If polar molecules such as those of water are present, the addition compound represented by $H_2O(AB)H_2O$ might be formed; this could dissociate (1) into $H_2O \cdot A$ and $H_2O \cdot B$, and (2) these again into A , B , and H_2O . If each of the changes (1) and (2) required less energy than the direct change $AB = A + B$, the rate of dissociation would be increased greatly by the presence of the polar molecules.

A similar effect might be produced by a surface on which AB could condense, forming addition compounds with the molecules at the surface, which we may denote by $S \cdot AB \cdot S$; these may dissociate into SA , SB , and these again into A , B , S .

The formation of these intermediate compounds may so accelerate the rate of reaction, that the difference between effects when they are present and when they are absent may be so large as to justify the statement that the presence of

the agents which produce these intermediate compounds is necessary for the chemical reaction.

As the effects produced are so large, a very small quantity of these intermediate compounds may produce a very pronounced effect on the reaction.

It is necessary to be alive to the fact that even when we are dealing with such an apparently simple case as a monomolecular reaction the actual processes involved may be much more complex than those which appear on the surface. Thus, for example, the reaction investigated by Cohen on the decomposition of As. H_3 by heat (*Zeitsch. Physik. Chem.* xxv. p. 483) is often cited as a proof that gaseous dissociation cannot be produced by collision, since Cohen found that it was not measured by the presence of a neutral gas. It is probable, however, that the dissociation took place at the sides of the vessel, since the nature of these surfaces had a great effect on the velocity of the reaction. If this is so, we should not expect the rate to be affected by the presence of a neutral gas, and the experiments do not touch the question whether or not collisions may in certain cases produce dissociation.

Summary.

The paper contains investigations—

(1) On the rate of recombination of positive and negative ions, it is shown that the coefficient α is, at not too high pressures, given by the equation

$$\alpha = \pi d^3 (U_+^2 + U_-^2)^{\frac{1}{2}} \left(\frac{1}{\lambda_+} + \frac{1}{\lambda_-} \right),$$

and at high pressures by

$$\alpha = 2\pi d^{\frac{3}{2}} (U_+^2 + U_-^2)^{\frac{1}{2}},$$

where d is given by the equation $e^2/d = \beta\theta$, where $\beta\theta$ is the energy of an atom of a monatomic gas at the absolute temperature θ , U_+ and U_- the average velocities of the polar and negative ions, λ_+ and λ_- the energy free-paths of these ions. It follows from these expressions that when the pressure is low, α is proportional to the pressure, which is in accordance with Thirkill's experiments. At higher pressures α should be independent of the pressure. The numerical value

for α for air at 0°C . and 760 mm. given by the preceding expression is in very fair agreement with the value found by observation.

(2) The values for λ_+ and λ_- are not the same as λ for an uncharged molecule: it is shown that λ_+/λ is a function of $(w/\beta\theta)^{\frac{1}{2}}$, where $\beta\theta$ is the same as before and w is the work required to separate a charged ion from an uncharged molecule with which it is in contact.

(3) When the negative charge is carried by electrons, special consideration is required in consequence of the disproportion between the masses of the electron and the molecules with which it comes into collision. It is shown that the energy free-path of an electron is exceedingly long, unless the energy of the electron when in collision with an electron in a molecule of the gas is comparable with the ionizing potential of the gas.

An expression is found for the rate of recombination of an electron and a positive ion.

(4) The rate of formation of complex ions is investigated, as well as the proportion between simple and complex ions when the gas is in a steady state. It is found that the condition that the ions should be mainly complex is the same as that for the free-path of an ion being much less than that of an uncharged molecule. Expressions are found for the periods which elapse before a simple positive ion becomes a complex one or an electron becomes a negative ion: the values obtained for the latter are of the same order as those found by Loeb in his experiments on this point.

(5) In the latter part of the paper the same principles are applied to Chemical Combination. Expressions are found for the rate at which two gaseous systems A and B combine, and also for the rate at which the compound AB dissociates. If p and q are the number of units of A and B respectively in unit volume, αpq the number which recombine per second, α is given by an expression of the same form as that for the coefficient of recombination of positive and negative ions, and at not too high pressures is proportional to the pressure. The rate of decomposition of the gaseous compound AB is determined on the hypothesis that it is due to collisions with the molecules of the gas; the objections which have been urged against this type of dissociation are shown not to be valid when the combination takes place in the way we have supposed.

(6) The effect of polar molecules in hastening chemical

combination by promoting the formation of polar molecules is investigated and found to be very large.

(7) An expression for the rate of monomolecular reactions in solids such as that of sublimation is obtained, and the great influences of surfaces such as the walls of the vessel in which the gas is contained on the rate of chemical reaction is indicated by the investigation.

Monomolecular reactions are regarded as due to the accumulation of thermal energy in particular molecules until these have sufficient energy to dissociate or evaporate as the case may be. Maxwell's law of the distribution of energy among the molecules of a gas expresses the fact that owing to collisions the energy accumulates in some molecules until it reaches a value far above the normal, though naturally the number of molecules which have energy much in excess of the normal diminishes rapidly as the excess increases. In gases the accumulation of energy is due to the collision among the molecules of the gas. In solids where the molecules form connected space-lattices the transference and accumulation of energy is due to pulses of displacement of molecules travelling in great number through the solid and producing by superposition effects whose magnitudes are governed by the same principles as those which determine the resultant amplitude of a large number of vibrations of arbitrary phase.

The expression for the rate of the monomolecular reaction contains two factors, one expressing the number of molecules which have the energy necessary for the change: this factor is of the form $e^{-Q/R\theta}$, where Q is this energy and θ the absolute temperature; the other factor expresses the rate at which molecules enter or leave the state. In gases this rate is inversely proportional to the time between two collisions, *i. e.* directly proportional to the number of collisions made by a molecule per second; in air at 0°C . and 700 mm. pressure this would be of the order 5×10^9 . In solids the time concerned is the duration of the passage of a pulse of light whose thickness is 10^{-3} cm. at 0°C . over a molecule; this is $1/3 \times 10^{13}$ seconds, and the rate factor is 3×10^{13} : thus these reactions would tend to go on much more rapidly at the surface of solids than in the body of a gas.

XXX. *The Motion of Electrons in Neon*, By V. A. BAILEY, M.A., D.Phil., Oxford, Associate Professor of Physics, University of Sydney*.

1. **I**N the account of experiments on the motion of electrons in argon and in helium recently published in the Philosophical Magazine † by Professor Townsend and myself, we gave a description of the methods used to investigate these gases. The same apparatus has now been used for the investigation of the behaviour of electrons in neon.

A quantity of neon containing about 1 per cent. of helium was very kindly supplied by M. Georges Claude, of Paris. No attempt was made to remove any of the helium, as this requires the use of liquid hydrogen, but all the common impurities were removed by passing the gas over charcoal at liquid-air temperature, before admitting it into a glass reservoir.

The measuring apparatus was tested for gas-tightness over a period of four weeks and found to have no perceptible leak in that time.

It was considered advisable to purify the gas again by passing it through a small charcoal tube interposed between the reservoir and the measuring apparatus and immersed in liquid air. The gas was generally kept in contact with the charcoal for about an hour before being admitted to the apparatus.

The same precautions as before were taken to prevent access of mercury vapour to the measuring chamber.

2. The experimental results are given in Table I., with the following notation :—

- p the gas pressure in millimetres of mercury,
- Z the electric force in volts per centimetre,
- W the velocity of the electrons in the direction of the electric force, in centimetres per second,
- k the factor by which the energy of agitation of the electrons exceeds that of an equal number of gas molecules at 15°C .

* Communicated by Prof. J. S. Townsend, F.R.S.

† Phil. Mag. Nov. 1922 and Oct. 1923.

TABLE I.

p .	Z .	Z/p .	k .	$W \times 10^{-5}$.
80	4.28	.0535	21.2	3.25
80	6.4	.08	29.5	3.50
80	8.56	.107	36.6	4.08
80	17.1	.214	65.3	5.10
40	8.55	.214	66.5	5.12
80	25.5	.32	93.5	...
80	34.2	.428	119	...
40	17.1	.428	122	6.55
40	25.5	.64	167	8.1
37	25.5	.69	180	...
40	34.4	.86	198	10.3
20	17.2	.86	183	...
20	25.8	1.29	225	16.5
20	34.3	1.72	264	22.9
10	17.2	1.72	234	...
10	34.3	3.43	304	46.0
5.05	17.0	3.36	258	...
5.15	34.3	6.67	320	81.0
2.5	17.0	6.8	310	...

Each of these results is the mean of several determinations made with different samples of the gas, the following set being typical:—

p .	Z .	Z/p .	k .	$W \times 10^{-5}$.
80	17.2	.215	66.7	5.35
80	17.2	.215	63.0	5.18
80	17.2	.215	64.5	5.04
80	17.0	.212	65.4	5.05
80	17.0	.212	66.6	4.90

The method of determining k and W is illustrated by the following example, the electrodes on which the stream of electrons was received being arranged as shown in figs. 1 and 2 in the paper on argon*. For $p=80$ and $Z=17$ it was found that the fraction $R=.329$ of the stream of electrons settled on the middle electrode, and that a magnetic force of strength $H=250$ was necessary to divert the centre

* Phil. Mag. Nov. 1922, p. 1035.

Fig. 1.

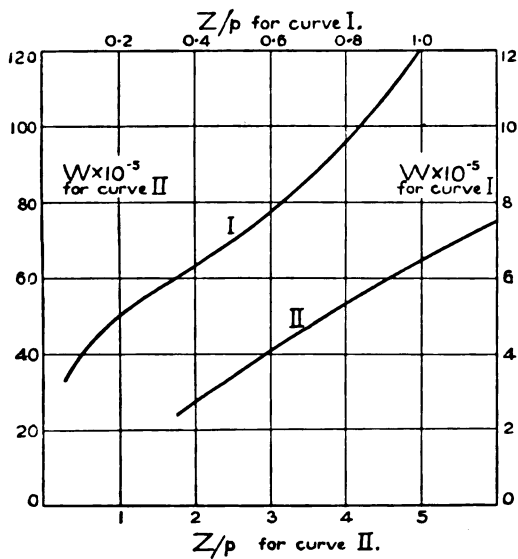
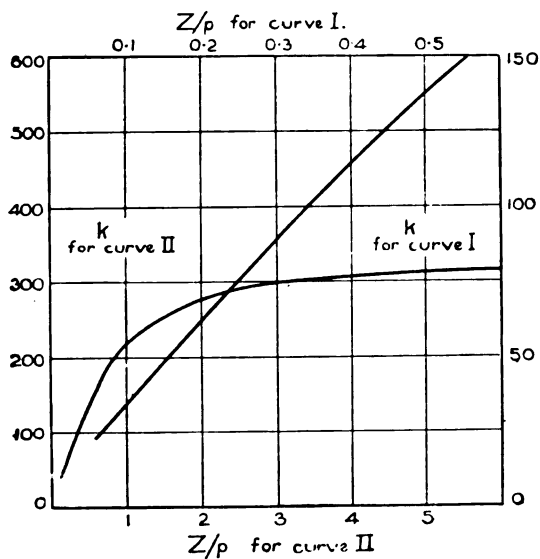


Fig. 2.



of the stream to the nearer air-gap. From the Standard Distribution Curve* it is seen that the ratio Z/k has the value $\cdot 260$ for $R=\cdot 329$, so the value of k is determined to be $65\cdot 4$. The velocity W is calculated by means of the formula $WH/Z=\tan \theta$, θ being the angle of deflexion of the stream due to the magnetic force H . Preliminary experiments having given the value $\cdot 0742$ for $\tan \theta$, W is thus found to be $5\cdot 05$.

The results given in Table I. are represented by the curves in figs. 1 and 2, which give the values of W and k for different values of the ratio Z/p .

3. In Table II. are given the values of the mean velocity of agitation u of an electron, its mean free path l at 1 mm. pressure of gas, and the proportion λ of the energy of an electron which is lost in a collision with a molecule, these three quantities having been calculated from the above values of W and k by means of the formulæ

$$u = 1\cdot 15 \sqrt{k} \times 10^7 \text{ cm./sec.}$$

$$l = (7Wu/Z) \times 10^{-16} \text{ cm.}$$

$$\lambda = 2\cdot 46 W^2/u^2.$$

TABLE II.

Neon containing 1 per cent. of helium.						Pure Neon.	
Z/p .	k .	$W \times 10^{-5}$.	$u \times 10^{-7}$.	$l \times 10^2$.	$\lambda \times 10^5$.	$l_n \times 10^2$.	$\lambda_n \times 10^5$.
$\cdot 06$	23.5	3.3	5.58	21.5	8.6	22.3	7.9
$\cdot 1$	34.5	3.95	6.75	18.7	8.4	19.3	7.8
$\cdot 2$	62.0	5.0	9.05	15.8	7.5	16.2	6.9
$\cdot 3$	89.0	5.72	10.85	14.5	6.85	14.8	6.3
$\cdot 4$	114	6.35	12.3	13.7	6.6	14.0	5.8
$\cdot 5$	137	7.05	13.5	13.3	6.7	13.5	5.8
$\cdot 6$	158	7.95	14.5	13.4	7.4	13.3	5.5
$\cdot 8$	194	9.65	16.0	13.5	9.0	13.7	6.9
1.2	235	15.0	17.6	15.4	17.9	15.6	...
2.0	275	27.0	19.1	18.0	49.0	18.3	...
4.0	308	53.0	20.2	18.7	170	19.0	...
6.0	316	74.5	20.4	17.7	330	18.0	...

* *Ibid.* p. 1039, fig. 3.

4. The proportion of helium present in the gas was determined by comparing the density of the latter with the known density of pure neon. The density of the gas was found by weighing it in a 250 c.c. flask and also weighing dry air (free from CO_2) in the same flask. It was found to be $\cdot 690$ of the density of air, and since the corresponding ratio in the case of pure neon is known to be $\cdot 696$, it follows that the gas contains 1 per cent. by volume of helium.

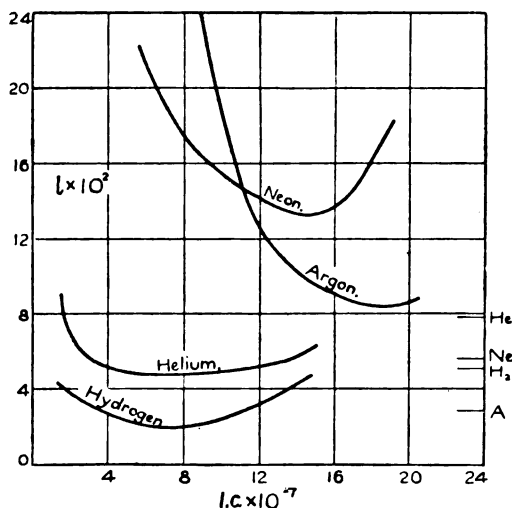
The values of l and λ for pure neon may now be calculated from those given in the fifth and sixth columns of Table II. by means of the formulæ

$$1/l = \cdot 01/l_h + \cdot 99/l_n,$$

$$\lambda/l = \cdot 01 \lambda_h/l_h + \cdot 99 \lambda_n/l_n,$$

where l_h, λ_h are the values of the free path and the fraction of energy lost for helium which were published recently*, and l_n, λ_n are the corresponding quantities for pure neon.

Fig. 3.



Values of l_n and λ_n calculated in this way are given in the last two columns of Table II., and those of l_n are represented by a curve in fig. 3. For purposes of comparison the curves for hydrogen, helium, and argon are also given in this figure.

* Phil. Mag. Oct. 1923.

It may be noticed from fig. 3 that for velocities u less than 10^8 the free paths are in the same order of magnitude as the atomic numbers. The lengths of the free paths deduced from viscosity measurements are indicated by short horizontal lines on the right border of fig. 3, and these are seen to be entirely different from the values deduced directly from the motion of the electrons. This emphasizes the dangers of the common practice of assuming values for the free paths of electrons which are deduced from measurements of viscosity, and also of assuming that they may be taken as independent of the velocity.

For each gas there is a range where l increases considerably as u diminishes, a property which has been shown to exist also for nitrogen, oxygen, carbon dioxide, carbon monoxide, and nitric oxide.

All four gases have minimum values of l , which correspond to velocities of about 1.4, 1.4, 5.7, and 9.6 volts for hydrogen, helium, neon, and argon respectively.

If it were assumed that the collision between an electron and an atom of an inert gas resembles that between two perfectly smooth and elastic spheres of masses m and M respectively, a simple calculation shows that the value of λ should be $2m/M$. In the case of helium, neon, and argon this ratio has the values 27×10^{-5} , 5.4×10^{-6} , and 2.7×10^{-5} respectively, which agree with the lowest of the experimental results as far as the order of the quantities is concerned. But this approximate agreement must not be taken as indicating that the collisions are to be treated as if the electrons collided with elastic spheres of fixed diameter, for the results show that with the smaller velocities there are many collisions in which the electrons are not appreciably deflected, and, if these collisions were taken into consideration in estimating the average fraction of energy lost in each collision, the values of λ obtained would be much smaller than the numbers given in this and in the previous papers to which I have referred.

This investigation has been carried out in Professor Townsend's laboratory, and I am also indebted to him in many other ways which assisted it to a successful termination.

XXXI. *The Mass-spectra of Chemical Elements.*—Part V.
Accelerated Anode Rays. By F. W. ASTON, D.Sc.,
 F.R.S., Fellow of Trinity College, Cambridge *.

THE last communication of this series† contained a description of work carried out up to the end of 1922. It was there pointed out that the difficulties in the way of extending the method of mass-spectrum analysis to other elements lay not so much in the analysis as in the production of their mass-rays‡. It was particularly desirable that a method should be evolved to give the mass-rays of the metallic elements which form so much the greater number of those not yet analysed. In this connexion it is of interest to note that, of all the ordinary non-radioactive non-metallic elements, only one, Tellurium, had failed to give a mass-spectrum.

Experiments with a Vacuum Arc.

The first essay in this direction was an attempt to draw out the ions formed in a vacuum arc between metallic points. The writer is indebted to Professor Merton for this suggestion, and also for advice as to possible means of carrying it out. An arrangement was made by which a heavy current could be automatically interrupted between a vibrating iron wire and the extreme edge of a stationary brass plate. The use of these metals insured the presence of at least three different types of ions all of reasonable mass. The device was simply a modification of the old Ruhmkorf interrupter, and the arcing was increased by introducing an inductance into the circuit. After a few trials it was found possible to maintain a strong discontinuous arc in a high vacuum for considerable periods. This arc was placed a few millimetres away from the pierced cathode of any ordinary parabola positive ray analyser, and its position carefully adjusted until it was exactly in line with the fine tube. The whole of the apparatus producing the arc was now maintained at a high potential of 20 to 30 kilovolts above that of the earthed cathode by means of a coil and rectifying valve. It was hoped that by this means some of the positive ions would be attracted out of the arc by the powerful electric field, and

* Communicated by the Author.

† Phil. Mag. xiv. p. 934.

‡ The term "*mass-rays*" has been suggested by Andrade ('The Structure of the Atom,' p. 83) to cover all swiftly moving particles of matter other than electrons. It therefore includes canalstrahlen, positive rays, anode rays, etc., each of which has a more limited meaning. The term seems admirably suited to its purpose, and in my opinion is a very welcome addition to the vocabulary of the subject.—F. W. A.

Phil. Mag. S. 6. Vol. 47. No. 278. Feb. 1924. 2 C

would form a stream of mass-rays directed down the fine tube of the analyser.

Many experiments were made, some with very prolonged exposures, but in no case was any trace of a parabola detected, and the method was reluctantly abandoned as impracticable. This is unfortunate, for had it succeeded it would doubtless have been as generally applicable as the arc in the optical spectra. The reason for so complete a failure is not obvious, but it is possible that though the abstracting field was of the order of 100 K.V. per cm., the local fields in the arc may have been even greater.

Experiments with Anode Rays.

After this set back the only remaining hope appeared to lie in anode rays. Of the two methods for producing these rays, described in the pioneer work of Gebrücke and Reichenheim, one, the Hot Anode method, had already been applied to the mass-spectrograph, but, although by its means the composition of the alkali metals* had been ascertained, it gave little hope of wider development. The other, which made use of a Composite Anode composed of a mixture of graphite and metallic salts, gave more promise, as it had already been applied with success by G. P. Thomson to the parabola method of analysis in the case of the lighter elements of groups I. and II.† A preliminary set of experiments was therefore undertaken to find out the best method of obtaining an intense beam of rays in a given direction under conditions suitable for use with the mass-spectrograph.

It is not intended to describe these experiments in detail. Discharge-tubes of a great variety in size and shape were tried, and the electrodes placed in all sorts of positions. Hot tungsten subsidiary cathodes were used in some cases in the hope of lowering the working pressure but without success. The same parabola analysis apparatus which had previously given the lithium parabolas‡ was employed in the tests. The same mixture of lithium, sodium, and potassium halides was used on the anodes, so that the relative efficiency of each type of apparatus could be quickly gauged by the visual brightness of the Li^+ parabola on the willemite screen. After a month of continuous work, a form of apparatus had been evolved which was capable of giving a strong visible lithium parabola continuously for several minutes. At this stage it was considered worth while applying the method to the mass-spectrograph.

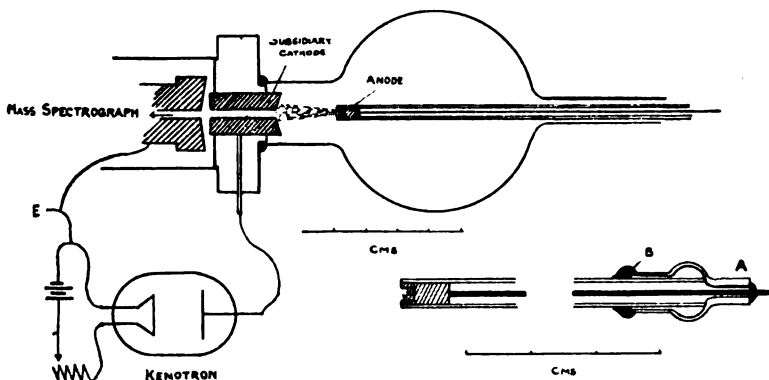
* Phil. Mag. xlii. p. 436.

† Phil. Mag. xlii. p. 857.

‡ Phil. Mag. xlii. plate xv.

Apparatus for accelerated Anode Rays.

The general form of the apparatus with which the best results were obtained is shown diagrammatically in the accompanying rough scale drawing. The discharge-tube is comparatively small and shaped as illustrated. The construction of the anode is indicated in detail on a larger scale. The graphite paste is pressed into a hole drilled in the end of a small steel cylinder. This is carried on a long brass wire so that it can be slid into a pyrex glass tube, about 20 cm. long, fitting it closely. The working position of the steel container is with its face containing the paste flush with the end of the tube, which is cut off exactly at right angles. The thickness of the walls of the container is exaggerated in the sketch. It is actually made as small as possible consistent



with strength, so that the anode looked at end on from the cathode appears simply as a graphite disk surrounded by a glass ring. Since the working of the apparatus is extremely capricious and liable to be altered entirely in character by the slightest variation in the position of its parts, it was essential that the anode container could be withdrawn, refilled, and replaced with great exactness. It was so arranged that when the glass cap A was pushed as far as it would go on the tube the container would be exactly in position. Withdrawal and replacement could be made any reasonable number of times by melting the wax joint B. The pyrex glass tube was carried in the long narrow neck of the discharge-bulb, and so held in position. The best working position of the anode was as indicated. The discharge producing the anode rays took place between the graphite paste and subsidiary cathode. The latter was an aluminium cylinder pierced for the passage

of the rays and hollowed at its working surface to concentrate the cathode rays on the anode. It was mounted in a block of ebonite just in front the earthed cathode of the mass-spectrograph*.

During the preliminary experiments when the cathode of the discharge-tube itself was earthed, it was found, in the first place, that good beams of anode rays could only be obtained when the pressure in the discharge-tube was comparatively high and the potential consequently too low to be convenient for use with the mass-spectrograph. In the second place, the discharge itself was exceedingly unstable, for increase of current meant a hotter anode; this led to the liberation of more gas, which caused further increase of current. On the other hand, if the anode was allowed to get too cold, the tube went hard and ceased to conduct altogether.

Both these difficulties were overcome by the introduction of a secondary cathode connected to earth through a kenotron as indicated. For if the earthed filament of the kenotron is maintained at a definite temperature—sufficient, for example, to give a saturation current of one milliamperere—it is impossible to force more than one milliamperere through it. Hence, whatever the conditions of the discharge-tube, short of absolute non-conductivity, the current through it will remain constant. It will be realized at once that this arrangement supplies exactly the stabilizing influence required. If the discharge-tube gets harder the potential drop between the anode and the subsidiary cathode will increase, hence the energy of the beam of cathode rays will increase; this will raise the temperature of the anode and soften the tube. On the other hand, if the tube gets too soft the energy of the cathode-ray beam will decrease, cooling the anode and hardening up the tube again.

In addition, the main discharge can now be regulated to give rays of any required energy independent of the hardness or softness of the discharge-tube. If we put a mean of 24 watts through the secondary circuit at a current of 1 milliamperere the anode will be maintained at a mean potential of 24 K.V. above earth, and the rays after leaving the subsidiary cathode will be *accelerated* to a velocity corresponding to that potential. Thus, if the potential between the anode and the subsidiary cathode is, say, 8 K.V., the accelerating potential will be 16 K.V.; if the discharge potential falls to 6 K.V. the accelerating potential will automatically rise to 18 K.V., and so on.

* *Phil. Mag.* xxxix. p. 613.

The kenotron with which the device was first tried was a high vacuum valve, made for an entirely different purpose, kindly lent by Dr. E. V. Appleton. For this experiment its grid and plate were connected together. This was later replaced by the simpler form of valve with no grid, shown in the sketch. These small kenotrons were kindly supplied by the M. O. Valve Co. The short straight filament only takes about 5 watts to heat and the kenotron behaves perfectly, working continuously for indefinite periods without any attention whatever.

Experimental Procedure.

The idea of the general working of the apparatus will be best conveyed by the description of a typical experiment performed after the conditions of the discharge-tube, position of the anode, etc., had already been shown satisfactory by preliminary photographs of the mass-lines of lithium. The first operation is the formation of the anode paste. The halide salt of the element to be studied is mixed with solid anhydrous lithium iodide and sometimes, in addition, other salts—such as lithium phosphate, potassium iodide, or sodium chloride—are added in small quantities. The mixture is pounded with about an equal weight of graphite powder—commercial stove polish, not graphite flakes—in a small agate mortar. After thorough incorporation the powder is moistened with a little saturated solution of lithium iodide, and the mixing and pounding continued very thoroughly with the resulting stiff paste.

Air is now admitted to the apparatus, the wax joint B melted, and the used container withdrawn and emptied. The freshly prepared paste is filled in and levelled to the rim. The container is now gently and cautiously heated over a bunsen flame to dry and consolidate the paste, the surface of which is smoothed from time to time. The heating is generally continued until iodine begins to come off in considerable quantity. The anode is then slid up to the end of the pyrex tube and the joint B remade.

Exhaustion is commenced as soon as the joint has set and its progress watched by passing a weak discharge with the kenotron short-circuited. At the same time the two charcoal tubes of the mass-spectrograph are heated. As the anode is heated up by the discharge water vapour is given off, shown by its typical violet discharge. After a time, generally a few minutes, the colour of the discharge changes abruptly to the dirty yellowish grey of iodine, the anode face glows with a brilliant red showing the lithium lines, and sometimes, but

not always, a bright divergent red beam of anode rays becomes visible. At this stage the discharge is stopped, the exhaustion continued with the Gaede pump to a very low point. Liquid air is applied to the charcoal tubes of the camera and slit system, the taps connecting these to the discharge-tube and pump are turned off, and the whole left for about half an hour to become completely exhausted.

The subsidiary cathode is now disconnected from earth and the kenotron put into action by heating the filament. The discharge is started by introducing a trace of gas, usually CO_2 , into the discharge-tube. The anode immediately heats up and the pump is started at once to remove gas as it is evolved, for if the pressure is allowed to get too high sparking may take place between the subsidiary cathode and the earthed cathode, short-circuiting the kenotron and destroying its stabilizing effect. As the current through the primary of the main induction-coil and the heating current of the kenotron filament are both completely under control, the current passing through the discharge and the potential of the anode can be set at any required values. These were usually 1 to 1.5 milliamperes and 24 to 30 K.V. When the appearance of the discharge is considered satisfactory the magnetic field of the mass-spectrograph is set, the plate exposed, and the exposure started by switching the electric field—usually 240 volts—on to the deflecting plates. The discharge cannot be stopped and started again like an ordinary gas discharge, for it and the heating of the anode are interdependent. If an accidental stoppage occurs the anode at once cools down and more gas must be introduced to start operations afresh. As the exposures are long the subsidiary cathode heats up considerably, and in order to prevent the melting of the wax joint surrounding it at the neck of the discharge-tube it is necessary to keep this under a continual air blast from a small fan.

It has not yet been found possible to obtain a beam of anode rays sufficiently strong for any mass-line to be visible on the willemite screen, as are the lines of hydrogen with the ordinary method. On this account the first three or four minutes of the discharge are generally utilized in recording the lithium lines as a necessary check on the working of the whole apparatus. The deflecting plates are then earthed, the photographic plate moved to a fresh position, and the magnetic field set for the element under investigation. The exposure is started as before by switching on the electric field, the discharge being maintained uninterrupted throughout these operations.

With all elements other than the alkali metals the effects are very faint, so the exposures are prolonged as far as possible until the anode dries up or it is judged that further continuation is useless. Most of the results, when the apparatus was working particularly well, were obtained with exposures of about half-an-hour, but in some cases the discharge was maintained for one hour and a half.

At the beginning of the discharge the anode surface is comparatively cool and glows brilliantly red, showing the lithium spectrum. The bright divergent beam of lithium anode rays never lasts many minutes of the exposure. Its appearance is a good sign, but equally bright lithium mass-lines have been obtained when it could not be seen at all. A valuable indication that the anode surface is functioning properly is the appearance of a small cloud of sodium light surrounding it, exactly as in the case of the Hot Anode experiments*.

As the gases come off less and less rapidly from the anode intermittent pumping only is required to keep the pressure down, and the latter and longer portion of the exposures is generally carried out without pumping at all. The anode by now has lost its lithium glow and becomes red and sometimes white hot. Lithium mass-rays are probably absent at these later stages, but the lines of the heavier members of the alkali group, if they are present in the anode paste, still continue to come off with the undiminished intensity, and in the case of other elements the high temperature of the anode surface seems favourable and may be essential. The general glow discharge, dirty yellow at the start, becomes blue-grey in the later stages.

Experimental Results.

The principal difficulty in the way of successful working of the method is complete ignorance of the mechanism of the discharge, which is probably very complex. It behaves at times in the most capricious and unaccountable manner. Each time the discharge-tube is altered or even taken down for cleaning entirely different results may be obtained. When by good fortune all is well the arrangement is capable of a surprisingly good performance. Thus, after a particularly favourable setting of the apparatus, six elements were successfully analysed in as many working days. On the other hand, when dismantling became imperative and it was cleaned and rebuilt—exactly as before, as far as one can tell,—no results of any value were obtained during weeks of work.

* Phil. Mag. xlii. p. 438.

Under these conditions any additional uncertainty in the procedure could not be tolerated, so schumannized plates, for which uniformity cannot be guaranteed, were only used when absolutely necessary. Normally the commercial half-tone plates were used, which are quite satisfactory for the detection of faint lines, as long as these are not too close to others. In their photographic intensities mass-lines obtained with anode rays cannot compare in any way with those obtained by the ordinary gaseous discharge, and are generally too faint for satisfactory reproduction. The pressure in the discharge-tube is relatively high, so that the vacuum in the slit system and camera is not so perfect. Also the exciting voltage found most suitable is not very high, and both these causes tend to render the lines obtained less sharp.

The method appears to be capable of very wide application to metallic elements. Those of Group I. are much the easiest to deal with and those of Group IV. apparently the hardest. The difficulty of obtaining the mass-rays appears to increase with increasing atomic weight, an effect which may be ascribed to decreasing velocity of the rays. The quantity of material necessary is only a few milligrams, of which much can be recovered after the experiment, so that it is particularly suitable in cases where only small quantities are available. High purity, as in other mass-spectrum measurements, is, in general, of quite subordinate importance.

In the matter of interpretation, the results of accelerated anode rays are very nearly ideal. The ordinary discharge-method gives altogether too many lines due to atoms and molecules other than those under consideration, the hot anode method gives too few, rendering measurement difficult. The new method gives practically no molecular lines at all, and the atomic ones generally present are just about what is required for a satisfactory system of reference, and no more. The most important of these lines are C^{12} , Al^{27} , Si^{28} , Fe^{56} , I^{127} . It is not difficult to recognize possible sources for these lines, but it is a rather strange thing that iodine should always give a strong line, while those of the other halogens are seldom perceptible, even though they are present in the anode in much greater proportion.

Experiments with the Light Elements.

The first use to which the new method was put was to obtain accurate mass-measurements of the isotopic constituents of some light elements, the constitution of which had already been determined by other and rougher methods. It

was considered very probable that the masses of these might differ from whole numbers by a greater percentage than those of the heavier ones.

Lithium.—The lines of this element, as has already been stated, were used to test the working of the apparatus. In consequence, a very large number of mass-spectra were taken showing the lines 6 and 7. They were obtained under a great variety of discharge-conditions, but in no case was any variation in their relative intensity observed. This is very strong evidence that the variation in relative intensity observed by G. P. Thomson * and Dempster † must have been a spurious effect. The later work of Dempster on the relative intensities of the components of zinc suggests that in his case the error was an instrumental one ‡. Measurements of both the lithium lines were made on a number of plates where they could be compared with the carbon line, which was assumed to be 12 exactly. The eight best measurements of the heavier isotope gave a mean value 7.006 ± 0.005 . The four best of the lighter gave 6.008 ± 0.005 . The deviation is in the direction expected for a nuclear packing looser than that of helium, but it is in neither case much more than the error of experiment.

Beryllium.—G. P. Thomson § only obtained one parabola with this element, and decided that it was therefore simple with a mass-number 9, notwithstanding the fact that its chemical atomic weight was then taken as 9.1. His conclusion has been practically confirmed by the recent work of Hönigschmid, who gives the atomic weight as 9.018. In the present experiment an anode of beryllium fluoride mixed with a little lithium iodide and lithium phosphate was used. Long exposures were required to obtain the beryllium line strong enough for good measurements. Comparison with carbon ($C=12.000$) on one plate and with lithium ($Li^7=7.006$) on another gave values 9.003 and 9.001 respectively.

Magnesium.—The isotopes of this element have already been determined by Dempster, but since the arrangement of mass cannot with his method be carried out with accuracy it was of interest to check his results on the mass-spectrograph, particularly with regards to the whole-number rule. An anode mixture containing magnesium chloride was used, and with some difficulty the principal line of the elements, 24, was obtained and measured against Na^{23} . It showed no

* Phil. Mag. xlii. p. 861.

† Phys. Rev. xviii. p. 420.

‡ Phys. Rev. xx. p. 636.

§ Loc. cit.

measurable deviation from the whole-number rule; the effects were too faint for the lines of the two other constituents 25 and 26 to be seen.

Calcium.—This element, like magnesium, does not produce anode rays at all readily. Several experiments were made with it. In some the fluoride was used, in others the chloride, but in no case was the Ca^{40} line as strong as that of K^{39} , although potassium was carefully excluded from the anode mixture. The alkali metals are abnormally sensitive to this method, and it is possible that its source was the pyrex-glass. The weakness of the principal calcium-line precluded any possibility of detecting its exceedingly faint companion at 44, discovered by Dempster, but on the best of the spectra obtained the expected second-order line at 20, searched for without success by G. P. Thomson*, was distinctly visible. The first and second order lines of calcium, both lines of potassium, and the strong single lines of sodium and aluminium could all be compared on the same spectrum, and were found integrally related to each other within the error of measurement. We are therefore faced with the remarkable conclusion that the two isobaric atoms Ar^{40} and Ca^{40} probably do not differ in weight by one tenth per cent., although the structure of their respective nuclei *must* be different, for one contains two more electrons than the other.

GERMANIUM (At. Wt. 72.38).

To investigate this element the fluoride was used. It was made from a sample of pure oxide kindly supplied by Professor L. M. Dennis of Cornell University. The oxide was simply heated with strong hydrofluoric acid and evaporated to dryness. The exact chemical constitution of the resulting material is of little importance, it appeared stable at high temperatures, and when incorporated with alkaline halides worked very well.

The mass-spectrum of germanium consists of three lines—70, 72, and 74, of intensities very roughly estimated as proportional to 2 : 4 : 5. No variation from the whole-number rule was observed, so that these intensities agree fairly well with the chemical atomic weight. It will be noticed that Ge^{70} is isobaric with the weakest and heaviest component of zinc discovered by Dempster, and that Ge^{74} is isobaric with the very weak lightest isotope of selenium.

* *Loc. cit.* p. 862.

COPPER (At. Wt. 63.57).

For this element an anode of cuprous chloride, lithium iodide, and rubidium chloride was used. The last salt was added to provide reference-lines. The effects obtained from copper were faint, but very conclusive, as both in intensity and position its lines appeared exactly as statistical considerations had led one to expect. These lines are 63 and 65; they were measured against Rb^{85} on one side and Fe^{56} on the other, and show no measurable deviation from the whole-number rule. The ratio of their intensities was about 2.5 : 1, in good agreement with the chemical atomic weight*.

STRONTIUM (At. Wt. 87.63).

Many experiments were done with this element. Its chloride, bromide, and iodide were all tried. The last seems to work the best, and was used mixed with lithium iodide and a little lithium phosphate. Strontium gives a remarkably bright visible beam of anode rays which usually persists long after the red lithium beam has disappeared. Its mass-spectrum shows a single line at 88. This line is always accompanied by rather more penumbra than usual, but it has all the characteristics of a true single line. The chemical atomic weight suggests the presence of at least one lighter constituent, so the experiments were repeated with schumanized plates. On these the penumbra was greatly reduced, so that a close component of any reasonable intensity must have been detected. None was observed, and the mass-measurements, relative to the iodide line, though not quite so accurate as usual, make it impossible to suppose that the divergence from a whole number could be sufficient to account for the fractional atomic weight. It is therefore difficult to escape the conclusion that the accepted figure given above is too low.

COBALT (At. Wt. 58.97).

Anhydrous cobaltous chloride was employed and mixed with sodium chloride and the usual lithium salts. A trace of rubidium present gave a valuable reference-line. Cobalt is a simple element characterized by a line at 59, exactly as was expected from its atomic weight, taken in connexion with the

* In 'Nature,' July 7th, Dempster described some results obtained with his apparatus, which led him to the conclusion that copper had three isotopes all of even atomic weight. The relative intensities of these lines suggested that they were probably due not to copper but to zinc adventitiously present (*vide* 'Nature,' Aug. 4th). He has since accepted this as the most probable explanation.—F. W. A.

empirical rule connecting odd atomic number with odd atomic weight. Measurements of the line were made with reference to Fe^{56} and Rb^{85} , and showed no deviation from the whole-number rule.

SCANDIUM (At. Wt. 45.10)

The only source of this rare element which happened to be available was a sample of the pure aceto-acetate kindly supplied by Professor G. Urbain of Paris. A small quantity of this was boiled with nitric acid and then ignited. The resulting powder was then treated with hydrofluoric acid, evaporated to dryness, and mixed with potassium iodide and lithium iodide for treatment. On the mass-spectrum only one new line at 45 could be distinguished, which when compared with K^{39} appeared accurately integral. Although long exposures were given, this line was always faint, so that the presence of small quantities of another constituent, expected at 47, could not in any case have been detected. Scandium may, therefore, be regarded as consisting mainly of atoms of mass-number 45, but further work will be necessary to prove the presence or absence of a second isotope suggested by the fractional atomic weight.

MANGANESE (At. Wt. 54.93).

Manganese fluoride made by the action of hydrofluoric acid on the pure carbonate was used mixed with lithium iodide. The appearance of these bodies when they were mixed suggested that a reaction of some sort took place. The mixture worked unusually well as an anode, and during the first few minutes of the discharge gave a good visible beam of anode rays. Contrary to all expectations, the beam was yellow and showed the sodium line only without a trace of the usual ones of lithium. No reason can be given for this phenomenon, which is characteristic of the frequent capricious and unaccountable behaviour of the discharge. Manganese is characterized by one line of mass-number 55, as expected from its atomic weight. It was measured against the neighbouring line of iron and showed no measurable divergence from an integer.

The mass-number of manganese has one particular point of interest. It is the eighth term of the well-known recurring series 2, 3, 5, 8, 13, . . . All the preceding terms correspond to gaps in the list of mass-numbers known to exist*.

* 'Isotopes,' p. 111.

GALLIUM (At. Wt. 69·72).

Abortive attempts to obtain the mass-spectrum of this element by means of its volatile chloride have already been described. It was successfully attacked by means of the new method by the use of its fluoride made by the action of hydrofluoric acid on a very pure specimen of the hydrate, for which the writer is indebted to Professor T. W. Richards of Harvard. The results obtained were faint, but gave satisfactory proof that the element consists of two components of mass-numbers 69 and 71. The intensity relation between the two lines agrees much better with Richard's recent determination of the atomic weight quoted above than with the value 70·1 previously in use.

VANADIUM (At. Wt. 50·96).

An anode consisting of vanadium chloride mixed with a little lithium iodide gave satisfactory results. A single line appeared at the expected position corresponding to mass-number 51. This was compared with K^{39} on the one side and with Fe^{56} on the other, and showed no measurable variation from a whole number.

CHROMIUM (At. Wt. 52·01).

The first experiments with this element were unsuccessful, but a second attempt during the period already alluded to when the experimental conditions were abnormally good succeeded at once. An anode containing chromium chloride, commercial chromium fluoride, and the usual lithium salts was used. The discharge after a few minutes became a rather unusual violet in colour and the anode was at a bright red heat throughout the entire exposure of 35 minutes. The single chromium line at the expected mass-number 52 was rather faint but unmistakable. Its integral value was established by comparison with Fe^{56} .

TITANIUM (At. Wt. 48·1).

The production and identification of the mass-rays of this element present quite peculiar difficulties. The failure of experiments on its volatile chloride by the ordinary discharge-method has already been described in these reports. It belongs to a chemical group which appears to be the least favourable to the production of anode rays. In the first attempts made with the new method potassium titanifluoride was employed. On the mass-spectra produced faint indications of a line at 48 could be seen, but were valueless for

the following reason. A fairly strong line appeared at 47. This was undoubtedly due to Si^{28}F , so that part if not all the effect at 48 could be ascribed to Si^{29}F . A later experiment in which the fluoride made by the action of hydrofluoric acid on the pure oxide was more successful. This gave a line at 48 not only reasonably strong but much stronger than that at 47, now feeble, so that there is little doubt that the principal constituent of titanium has a mass-number 48. On one spectrum a very faint ghost could be distinguished at 50. If this should prove to be a true isotope, it would tend to support Hönigschmid's value of the atomic weight given above, rather than the lower value 47.88 more recently suggested by Baxter.

SILVER (At. Wt. 107.88).

An anode containing silver chloride and lithium chloride, though behaving rather unsteadily as regards discharge, gave a very definite result. Silver has two isotopes, whose mass-lines when measured against that of iodine have integral values 107 and 109. The first of these is slightly the brighter. Owing to the weight of accumulated statistical evidence in connexion with the relation between odd atomic number and odd atomic weight, and the exceptional trustworthiness of the chemical atomic weight work on silver, this result might be described as a foregone conclusion.

YTTRIUM (At. Wt. 88.9).

A small quantity of this rare element in a state of metallic powder was dissolved in hydrofluoric acid. The resulting fluoride worked quite well when mixed with lithium iodide. The mass-spectrum showed one line only, which, when compared with I^{127} , gave a value 89 integral within experimental error. It will be noticed that this number is the ninth term in the series mentioned under manganese. The success of the method in generating the mass-rays of scandium and yttrium holds forth hopes of its applicability to all the rare earth elements.

Experiments with Zirconium and Hafnium.

The new element hafnium presents a unique opportunity of determining the atomic weight by the mass-spectrograph before any satisfactory value has been obtained by chemical means. Unfortunately, the titanium, zirconium, hafnium group appears the most difficult to tackle of all, so far as production of mass-rays is concerned. The first experiments on zirconium were done with a fluoride made by dissolving in hydrofluoric acid a small quantity of a rich mineral zircon,

kindly supplied by Dr. Dootson. Even with the longest exposures no reliable indication of the zirconium lines could be seen, though on one plate a doubtful trace could be distinguished at 90, which may have been due to the main constituent of the element. It was already realized that increase of atomic weight decreases the chance of getting mass-lines, so that this result extinguished all reasonable hope for the much heavier element hafnium. As, however, Dr. Hevesy had been kind enough to supply a sample of potassium hafnium-fluoride, estimated to contain about 50 per cent. zirconium-fluoride, a careful trial was made with this material. As had been feared, no lines in the region 178 could be seen at all, though again there was the suggestion of a line at 90, possibly zirconium. It is hardly necessary to state that this failure does not suggest in the slightest degree that hafnium was not present. It only indicates a conclusion, which further experiments with pure zirconium fluoride have confirmed, that it will be exceedingly difficult to obtain satisfactory mass-spectra of these elements.

Other Experiments yielding Negative or Inconclusive Results.

Experiments with niobium, molybdenum, cadmium, and lead have so far given no indication whatever of the mass-lines of these elements. The results with barium were not entirely negative, since a slight effect was visible on the plate in the expected position. This suggested that barium has several isotopes, and there is little doubt that its composition could be determined if a sufficiently advantageous setting of the discharge-tube could be made. Attempts to get the principal line of iron 56 so strong that the presence or absence of the possible weak component 54 could be established have so far been unsuccessful.

Table of Results.

Element.	Atomic Number.	Atomic Weight.	Minimum Number of Isotopes.	Mass-numbers in Order of Intensity.
Se	21	45.1	1	45
Ti	22	48.1	1	48
V	23	51.0	1	51
Cr	24	52.0	1	52
Mn ...	25	54.93	1	55
Co	27	58.97	1	59
Cu	29	63.57	2	63, 65
Ga	31	69.72	2	69, 71
Ge	32	72.5	3	74, 72, 70
Sr	38	87.63	1	88
Y	39	88.9	1	89
Ag	47	107.88	2	107, 109

If one adds these results to the table given in the previous report of this series * it will be seen that the first thirty-nine elements in sequence have been analysed and, in addition, seven more of higher atomic number, so that the constitution of rather more than half the known elements has been established, in most cases with considerable certainty. The new results given in this paper strengthen the empirical laws observed to hold relating to the connexion between atomic number and atomic weight. In the case of the elements of odd atomic number, the rule that they cannot have more than two isotopes still shows no exception, and the law that their atoms should have odd atomic weight is satisfied by all the elements in the list given above. The only exceptions to the latter law, which means that the nuclear electrons are always associated together in pairs, are nitrogen and the two weaker isotopes of lithium and boron, all very light elements. In a curiously large number of cases a difference of atomic weight 44 is connected with a difference of atomic number 18, and gives a pair of elements having similar chemical properties, as the following list indicates :—

Mg 24 Mg 26 Al 27 Si 28 Si 30 P 31 S 32 Cl 35 Cl 37 Ar 36 Ar 40
 Zn 68 Zn 70 Ga 71 Ge 72 Ge 74 As 75 Se 76 Br 79 Br 81 Kr 80 Kr 84
 Ca 44 Sc 45 Cu 63 Cu 65.
 Sr 88 Y 89 Ag 107 Ag 109.

In conclusion, the writer wishes to thank Sir William Pope for placing at his disposal for this work a great variety of metallic compounds, and to Mr. Stokeley for his valuable personal assistance in this connexion. He also wishes to repeat his acknowledgment to the Government Grant Committee of the Royal Society for part of the apparatus employed in this research.

Summary.

A new method of producing anode rays suitable for mass-spectrum analysis is fully described, together with experiments which led to its development.

By its means the principal isotopes of lithium, beryllium, magnesium, and calcium are shown to have atomic weights closely approximating whole numbers.

Experiments are described by which the constitution of twelve more metallic elements has been determined and a list of these and their isotopes is given.

Cavendish Laboratory, Cambridge,
 November 1923.

* Phil. Mag. xlv. p. 944.

XXXII. *Ionization by Collision in Helium.* By J. S. TOWNSEND, M.A., Wykeham Professor of Physics, Oxford, and T. L. R. AYRES, M.Sc., D.Phil., Exeter College, Oxford*.

1. **T**HE experiments with helium which are described in this paper were made in order to determine the conditions under which the gas is ionized when electrons collide with molecules. They also provide a means of testing some of the various views of physicists on effects which may be produced when electrons with certain critical velocities collide with molecules of the gas.

We have been unable to reconcile the results of the experiments with the recent theories, and we find that the original theory of ionization by collision which was given many years ago affords a satisfactory explanation of the experiments. This theory was found by Gill and Pidduck † to be in good agreement with their experiments on the currents through monatomic gases obtained when electrons are set free from the negative electrode and move through various distances to the positive electrode under a uniform electric force.

It has been considered desirable to repeat these experiments with helium, and to extend the investigations in order to find the conditions under which the first set of additional electrons are generated by the electrons set free from the negative electrode. The results thus obtained provide a means of calculating the average velocities of electrons before and after the collisions with the molecules which are ionized. The method of finding these velocities and the energy required to ionize a molecule has already been explained in a paper recently published in the 'Philosophical Magazine' ‡.

The method was there applied to the results of a set of experiments in which the ratio of the electric force X to the gas-pressure p was 16, X being in volts per centimetre and p in millimetres of mercury, and it was found that the amount of energy required to ionize a molecule of helium was less than the energy acquired by an electron in moving between two points differing in potential by 14 volts. A large number of additional experiments have recently been made,

* Communicated by the Authors.

† E. W. B. Gill and F. B. Pidduck, *Phil. Mag.* (6) vol. xvi. p. 280 (1908), and vol. xxiii. p. 837 (1912).

‡ J. S. Townsend, *Phil. Mag.* vol. xlv. p. 1071 (May 1923).

taking various values of the ratio X/p , which are also in good agreement with the theory and confirm the result previously obtained as to the comparatively low value of the energy required to ionize a molecule of helium.

2. In order to find the velocities of electrons before and after the collisions in which molecules are ionized, it is necessary to examine certain stages of the development of the currents obtained between parallel plates when ultra-violet light acts on the negative electrode, and the distance x between the electrodes is varied while the electric force X and the gas-pressure p are constant.

A complete investigation may be considered to extend over three distinct stages. In the first stage, as the distance x between the plates is increased from zero up to a certain limit $x=a$, the mean energy of the electrons varies with the distance between the plates, and does not attain a final steady value until a considerable number of new electrons have been obtained by increasing x . In this stage it is convenient to represent the current in terms of the distance x or the potential difference Xx between the plates by a curve, as there is no simple formula representing the relation between the current and the potential.

In the second stage, from the distance $x=a$ to the distance $x=b$ the current is represented in terms of the distance x by the formula $n=n_0\epsilon^{\alpha x}$, which shows that the mean energy of the electrons and the distribution of the energies about the mean are the same in passing any plane parallel to the electrodes.

In the third stage, from the distance b up to the sparking distance the rate of increase of the current with the distance is greater than the increase of n as given by the above formula, and the current is given in terms of x by an equation of the form

$$n=n_0 \frac{(\alpha-\beta)\epsilon^{(\alpha-\beta)x}}{\alpha-\beta\epsilon^{(\alpha-\beta)x}}.$$

For the purpose of this investigation it is not necessary to find the currents for distances between the electrodes greater than b , or to determine the process of ionization which causes the rate of increase of the current with the distance to exceed the rate given by the formula $n=n_0\epsilon^{\alpha x}$. It may be stated that there are no definite values to be given to distances a and b , as the mode of development of the current changes gradually as the distance x is increased.

3. In the experiments that have been made with helium

every precaution has been taken to have the gas free from impurities. The apparatus containing the adjustable parallel plates was constructed with glass insulation throughout, as it was found that ebonite surfaces may introduce impurities which have an appreciable effect on the motion of electrons. The apparatus was perfectly air-tight, and when exhausted to $1/100$ of a millimetre pressure, it was impossible to detect any leak in the course of several days by means of a McLeod gauge. The method adopted to avoid mercury vapour was the same as that used in the experiments on the motion of electrons in helium which have recently been published*. As in the latter experiments, two specimens of helium were used, one obtained from a natural source and the other obtained by heating thorianite, and it was found that the effects due to ionization by collision were the same in the two specimens.

The plate electrodes were silver disks 6 cm. in diameter, the upper plate being carried by a micrometer screw in order that it might be set at any distance from the lower plate from 1 to 10 millimetres. The ultra-violet light from an external spark-gap passed through a quartz window in the base of the instrument and through narrow slits in the centre of the lower electrode, and fell normally on the upper plate which was the negative electrode. The slits in the lower electrode were about a centimetre long, a fifth of a millimetre wide, and 1 millimetre apart.

4. When the electric force X and gas-pressure p are constant, the currents i obtained with different distances x between the plates may be expressed by means of a curve in terms of the potential difference V between the electrodes. This curve remains unaltered when X and p are altered in the same proportion, but there is a different curve for each value of the ratio X/p . This result follows from the theory, and it has also been verified experimentally.

In any of these curves the ratio i_1/i_2 of the two currents corresponding to two given potentials V_1 and V_2 is independent of the number of electrons set free initially from the negative plate by the ultra-violet light. This result has been verified by changing the intensity of the light. All conclusions to be drawn from these curves must satisfy these conditions.

The currents were measured by an induction balance by a zero method, using a sensitive electrometer to indicate the

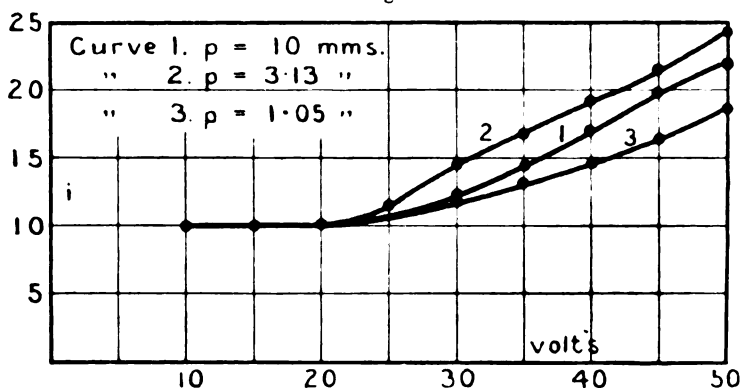
* J. S. Townsend and V. A. Bailey, *Phil. Mag.* vol. xlv. p. 657 (Oct. 1923).

zero potential. They were all small currents of the order from 10^{-12} to 3×10^{-11} ampere.

Although these simple facts, which have been verified by experiments of this type, have been mentioned in the account given of previous researches, we think it necessary to repeat them, as they have been lost sight of in some of the theories that have been suggested to explain ionization by collision.

5. Several curves have been determined which give the relation of the current to the potential difference between the plates for different values of the ratio X/p . Three examples of these curves are shown in fig. 1, the ordi-

Fig. 1.



nates being proportional to the currents and the abscissae proportional to the potential difference V between the plates or to the distance x between the plates, V being equal to Xx .

The same electric force X , 50 volts per centimetre, was used in determining the points on the curves. The distance between the plates was varied from 2 to 10 millimetres, so that the potentials of the positive plate were from 10 to 50 volts, the negative electrode being taken as the zero of potential. The first curve gives the currents in helium at 10 millimetres pressure, the second curve at 3.1 millimetres pressure, and the third curve at 1.05 millimetres pressure. Thus the values of the ratio X/p to which the curves correspond are 5, 16, and 47.5 respectively.

The ordinate 10 is taken to represent the current in each case when the plates are 2 millimetres apart. For each pressure the current was the same for the distances 2, 3, and 4 millimetres between the electrodes, so that the three curves coincide and are parallel to the x axis for the range of potentials from 10 to 20 volts, the currents consisting of the

electrons set free from the negative electrode by the ultra-violet light.

These electrons start from the negative electrode with a small velocity, and do not acquire sufficient energy to ionize the molecules of gas in appreciable numbers until after they have passed the plane where the potential is 20 volts. After passing this plane there is a continuous increase in the current, the rate of increase depending on the pressure of the gas.

If N be the number of electrons coming from the negative electrode, the number in the stream is $1.5 \times N$ as it passes the 36-volt plane, and the number is $2 N$ as the stream passes the 45-volt plane when the pressure of the gas is 10 millimetres.

When the gas-pressure is reduced to 3.13 millimetres, the number of electrons in the stream is $1.5 N$ in passing the plane at 31.5 volts, and the number is $2 N$ in passing the plane at 42 volts.

When the gas-pressure is further reduced to 1.05 millimetres, the rate of increase of the current with the distance between the plates is diminished, the number of electrons in the stream being $1.5 N$ in passing the plane at 41.3 volts and $2 N$ in passing the plane at 53.5 volts.

6. In explaining the curves in fig. 1, it is of interest to know approximately the number of collisions each electron makes with molecules of the gas in traversing a given distance in the direction of the electric force. The mean free path of an electron in helium at 3.13 millimetres pressure is about 1.7×10^{-2} centimetre. It is unnecessary to take into consideration the variation of the mean free path with the velocity, as we are concerned only with the order of this length. In traversing 1 millimetre in the direction of the electric force, the electron does not move in a straight path for this distance, as its direction of motion is changed in each collision. The total length of all the free paths of an electron exceeds the distance it travels in the direction of the electric force in the same proportion as the velocity of agitation exceeds the velocity in the direction of the electric force. Thus the total distance that an electron travels through the gas while it moves 1 millimetre in the direction of the electric force is more than 4 centimetres*.

* The mean free paths and velocities of electrons involved in this calculation are taken from the paper on "The Motion of Electrons in Helium" which has just been published (J. S. Townsend and V. A. Bailey, Phil. Mag. Oct. 1923). The determinations refer to a range of values of the ratio X/p lower than the range which includes the cases where ionization by collision produces large effects, so that the estimate of the number of collisions given above is only an approximate estimate for these ranges of forces and pressures.

Hence, in the above experiments at 3.13 millimetres pressure, an electron collides with more than 100 molecules of the gas in moving 1 millimetre in the direction of the electric force. Although an electron may lose only a small proportion of its energy in a collision with a molecule that is not ionized, there is a very large number of such collisions, and the total loss of energy due to this cause is quite appreciable. Since there are more collisions at the higher pressures than at the lower pressures, the effect of this loss of energy is greater at 10 millimetres than at 3.13 millimetres. The reduction in the rate of increase in the current with the distance between the electrodes, when the pressure is increased from 3.13 to 10 millimetres, is obviously due to this cause.

The reduction in the rate of increase in the current, when the pressure is reduced from 3.13 to 1.05 millimetres, must be attributed to another effect. In passing through a plane at any fixed distance from the negative electrode, the energy of the electrons is greater at the lower pressure than at the higher pressures, since there is less loss of energy in collisions in traversing the space between the negative electrode and the plane. Thus, when the electric force is constant, the energy of the electrons in the collisions with the molecules which are ionized increases as the pressure is reduced.

When the pressure is below the value corresponding to $X/p=16$, the number of molecules ionized per millimetre diminishes with the pressure. This shows that ionization by collision only occurs in a small fraction of the total number of collisions of an electron with molecules, even when the energy of the electron in each collision is sufficiently large to ionize a molecule. The rate of increase of the current with the distance between the electrodes is therefore reduced when the pressure is reduced from 3.13 to 1.05 millimetres, because the total number of collisions is reduced, and consequently the probability of ionization by collision is also reduced.

7. Let c be the energy required to ionize a molecule, $(c+r)$ the energy of an electron before a collision in which a molecule is ionized. The quantity c may be taken as a constant, but r varies over a wide range. Let $\bar{r}$ be the mean value of r for all the collisions in which molecules are ionized.

Let W be the loss of energy of an electron in the collisions with molecules which are not ionized in moving from the

negative electrode to the distance where it ionizes a molecule. The values of W vary over a wide range, since the values of δ and the number of collisions per centimetre is different for each electron. Let $\bar{W}$ be the mean value of W for all the electrons set free from the negative electrode.

If all the energies be expressed in volts, the energy of the electron when it is set free from the negative electrode is of the order of one volt, and it may be neglected in comparison with the principal quantities of energy which are being considered.

The electron acquires the energy $c + v$ in moving under the action of the electric force X through the distance δ , and it loses the amount W before arriving at the point where it ionizes a molecule. The following relation is obtained between the energies :

$$X\delta = c + v + W.$$

The curve 2 (fig. 1) giving the currents in helium at 3.13 millimetres pressure with the force of 50 volts per centimetre shows that a few of the electrons from the negative electrode ionize molecules before reaching the plane δ_1 , where the potential $X\delta_1$ is 21 volts, while others do not ionize molecules until the plane δ_2 is reached, where $X\delta_2$ is 42 volts, this being the plane at which the number of electrons in the stream is 2 N. Thus there is a wide divergence between the values of $v + W$ for the different electrons which indicates that the sum $\bar{v} + \bar{W}$ is also large.

The quantities $\bar{v}$ and $\bar{W}$ are functions of the ratio X/p , and the values of $c + \bar{v} + \bar{W}$ corresponding to different values of X/p may be obtained from the areas of the curves (fig. 1.)

Thus

$$c + \bar{v} + \bar{W} = \frac{1}{N} \int_N^{2N} V di = X\bar{\delta}. \quad (1)$$

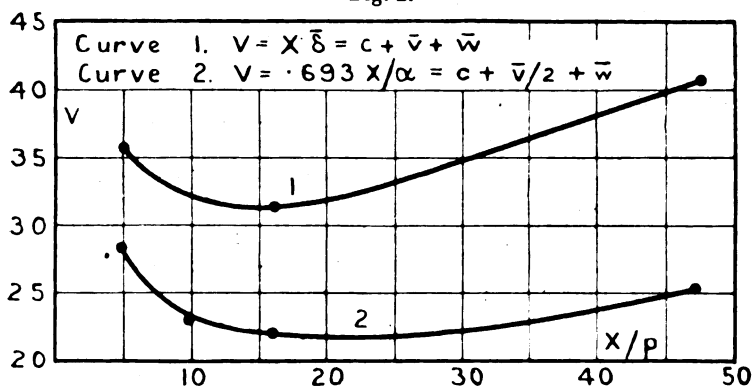
The mean potential $X\bar{\delta}$ is nearly the same as the potential at the point where the current is 1.5 N.

These potentials are represented by curve 1 (fig. 2) in terms of the ratio X/p , one point on this curve being obtained from each curve of the type shown in fig. 1.

8. The currents in the second stage of the process of ionization where the average velocity of the electrons is constant were determined with the same apparatus, using larger electric forces and gas-pressures. In this stage the

current is given in terms of the distance x between the plates by the formula $n = n_0 e^{\alpha x}$, and the value of α corresponding to any force and pressure is easily determined.

Fig. 2.



In these experiments the potential difference between the plates was generally less than 100 volts, so that no correction had to be made for effects due to other processes of ionization.

There is a considerable range of distances between the electrodes over which the currents in helium have been found to agree accurately with the above formula, and this result affords the principal reason for attributing the increase of current to the ionization of the molecules by the collisions of the electrons. If any other process contributed appreciably to the increase of current, there would be a large deviation from the formula. Within this range of distances between the electrodes the quantity α can be easily measured, and there is no appreciable error introduced by any other ionizing effect.

As it is necessary to be quite certain on this point, another investigation is being made in the laboratory to find by a more direct experimental method if there are other processes of ionization comparable with the direct effect of the collisions of electrons with molecules, when the ranges of potentials and pressures are the same as those used in the experiments on the determination of α . A full account of the investigation will be given in another paper, but it may be stated that the method was sufficiently sensitive to detect effects which might be due to ionization of molecules by the collisions with positive ions, or to electrons set free from the negative

electrode, either by impacts of positive ions or by radiation from molecules of the gas, but no effects due to these causes were observed under conditions where the currents were proportional to $e^{\alpha x}$.

The original theory of ionization by collision implies that ionization is due to one collision of an electron with an ordinary molecule, and that a certain relation must hold between the values of α , X , and p , which is expressed by the formula $\alpha/p = f(X/p)$. This relation has been tested with helium, and in the experiments where the ratio of the force to the pressure was constant the ratio α/p was also constant. If any appreciable effect arose from an impurity in the gas, this relation could only be obtained if the amount of the impurity were proportional to the pressure of the helium. The results of the experiments with different forces and pressures therefore show that it would be unreasonable to suppose that there is any appreciable error due to impurities, as it is extremely improbable that the amount of an impurity would increase with the pressure of the helium.

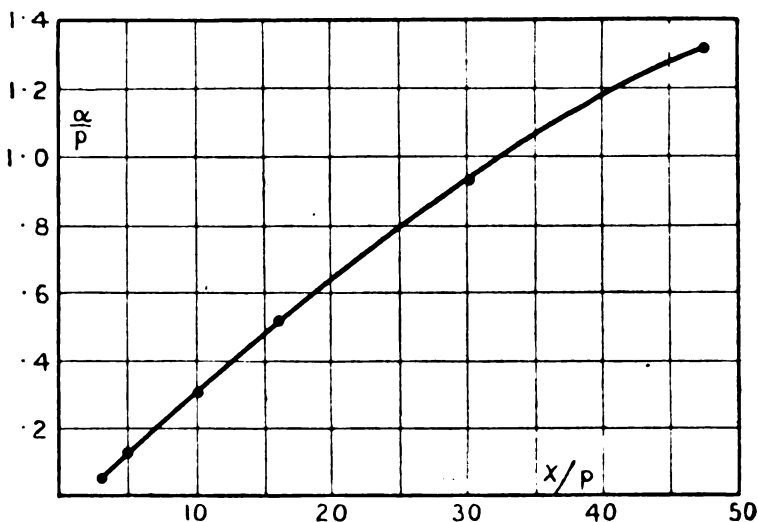
Also the factor $e^{\alpha x}$ is independent of the number of electrons in the current, as it was found that all the currents were changed in the same proportion when a large change was made in the number of electrons set free from the negative electrode by altering the intensity of the ultra-violet light.

If the ionization by collision in these experiments were due to two collisions of electrons with the same molecule, the number of electrons generated by collision would be proportional to the square of the current; but no change was observed in the values of α when the intensity of the current was changed in the proportion of 3 : 1, so that the experiments show quite conclusively that in each case where an electron is generated the molecule is ionized by a single collision.

9. The results of the experiments on the determination of α for helium may be represented in the usual manner by a curve giving the ratio of α/p in terms of X/p . The curve is given in fig. 3, and it shows that, if X be constant and p variable, α has a maximum value at the pressure for which the ratio X/p is the abscissa of the point of contact of the tangent from the origin, which is near the point $X/p = 16$. If X be 50 volts per centimetre, the maximum value of α is obtained when p is about 3.13 millimetres, α being 1.56. At the pressure 10 millimetres, $X/p = 5$ and $\alpha = 1.22$; and at the pressure 10.5 millimetres, $X/p = 47.5$ and $\alpha = 1.37$.

These changes in the value of α are due to the same causes as the changes in the value of $X\bar{\delta}$. With the largest pressure the number of molecules ionized per centimetre is small, owing to the loss of energy of the electrons in the collisions with other molecules. With the smallest pressure although the average kinetic energy of the electron is increased, the number of molecules ionized per centimetre is reduced, owing to the reduction in the total number of collisions with molecules.

Fig. 3.



10. The currents in this stage are given by the formula $n = n_0 e^{\alpha x}$; and if n_1 and n_2 be the numbers of electrons passing two planes at the distances x_1 and x_2 from the negative electrode, $n_2 = 2n_1$ when $e^{\alpha(x_2 - x_1)} = 2$. In this case the distance between the planes $(x_2 - x_1) = 0.693/\alpha$.

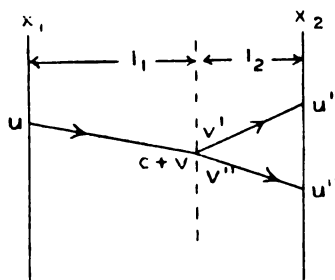
When an electron moving with the energy $c + v$ ionizes a molecule, the quantity of energy c is lost in separating the new electron from the molecule, and the remainder of the energy v is either retained by the original electron or divided between the two electrons. The mean energy of these two after the collision is therefore $v/2$.

In this stage the average value of $(c + v)$ for all the collisions in which molecules are ionized is the same as the average $c + v$ in the first stage, when the ratio X/p is the same in the two stages, provided $\bar{v}/2$ is not large compared with c

(or about 10 volts). Since the average energy of the electrons after collisions in which molecules are ionized is $v/2$, there is a wide divergence between the energies of the electrons in the stream, but the mean energy of the electrons passing any plane is constant. In the case of the two planes x_1 and x_2 where the numbers of electrons are n_1 and $2n_1$, the increase in the current with the distance is the same as if each electron passing the plane x_1 with energy u ionized one molecule in the space between the two planes and the mean energy of the two electrons as they pass through the plane x_2 is equal to u .

The average effect is represented by the diagram (fig. 4).

Fig. 4.



If an electron enters the space through the plane x_1 with energy u , its energy is increased to $(c + v)$ in moving the distance l_1 in the direction of the electric force X to the point where a molecule is ionized. The energy before the collision is given by the equation

$$c + v = Xl_1 + u - w_1; \quad \dots \quad (2)$$

w_1 being the energy lost by the electron in collisions with molecules which are not ionized while traversing the distance l_1 .

If v' and v'' be the energies of the two electrons after the ionizing collision, $(v' + v'')$ is equal to v , and after moving the distance l_2 where $l_1 + l_2 = x_2 - x_1$, their mean energy is equal to u . Let u' and u'' be the energies of the two electrons as they pass the plane x_2 , then

$$\left. \begin{aligned} u' &= Xl_2 + v' - w_2' \\ u'' &= Xl_2 + v'' - w_2'' \end{aligned} \right\}, \quad \dots \quad (3)$$

w_2' and w_2'' being the loss of energy of the two electrons respectively in collisions with molecules which are not ionized while they traverse the distance l_2 .

The mean energy which is equal to u is

$$\frac{u' + u''}{2} = Xl_2 + \frac{v}{2} - w_2,$$

where $w_2 = (w_2' + w_2'')/2$.

Thus $c + v = X(l_1 + l_2) + v/2 - (w_1 + w_2)$.

Since $l_1 + l_2 = x_2 - x_1 = \cdot 693/\alpha$, the following relation between the energies is obtained :

$$\frac{X}{\alpha} \times \cdot 693 = c + \frac{v}{2} + w, \quad . \quad . \quad . \quad (4)$$

w being the mean loss of energy of an electron in traversing the distance $x_2 - x_1$. The distance $\cdot 693/\alpha$ is the average distance measured in the direction of the electric force that two electrons move after the collision in which a molecule is ionized to the next collisions in which ions are again generated.

All the electrons do not act as indicated in fig. 4, since some of those entering the space between the planes x_1 and x_2 with small energies near the value $v/2$ may pass through without ionizing molecules, but the number passing out is made up to $2n_1$ by other electrons which enter the space with large energies near the value $c + v$ and ionize two molecules each. This does not alter the relation between the energies given by equation (4).

11. The quantities $\bar{v}$ and w are functions of the ratio X/p , and formula (4) represents the equation of the curve (fig. 3), giving α/p in terms of X/p .

The ratio X/α corresponding to different values of the ratio of X/p are found from the curve (fig. 3), and the quantity $(c + v/2 + w) = \cdot 693X/\alpha$ is given in terms of X/p by curve 2 (fig. 2), the potential $V = \cdot 693X/\alpha$ being in volts, X in volts per centimetre, and p in millimetres of mercury. Thus the two quantities $c + \bar{v} + \bar{W}$ and $c + \bar{v}/2 + \bar{w}$, corresponding to a series of values of the ratio X/p , are obtained directly from the experiments, the probable experimental error being about 2 or 3 per cent.

The difference between $\bar{W}$ and $\bar{w}$ is comparatively small. The quantity $\bar{W}$ represents the average loss of energy of an electron in collisions with molecules that are not ionized in moving from the negative electrode to the plane where its energy is $c + \bar{v}$. The quantity $\bar{w}$ is the average loss of energy of an electron under the same conditions in moving from a plane where its energy is $\bar{v}/2$ to the same plane where its energy is $(c + \bar{v})$. Thus the difference $(\bar{W} - \bar{w})$ is the loss

of energy of an electron in collisions with molecules in its path from the negative electrode to the point where its energy is $\bar{v}/2$. In this part of its path the kinetic energy of the electron is comparatively small and the velocity in the direction of the electric force is comparatively large. As it moves in the direction of the electric force, the kinetic energy (which is the energy of agitation) increases and the velocity in the direction of the force diminishes. Thus, in the first part of its path from the negative electrode, the loss of energy of the electron in each collision is small and the total number of collisions per millimetre in the direction of the force is also small, since the latter number is proportional to the ratio of the velocity of agitation to the velocity in the direction of the electric force.

For a first approximation, therefore, the quantity $(\bar{W} - w)$ may be neglected in comparison with $\bar{w}$.

The following table gives the values of $\bar{v}$ and $(c + \bar{w})$ in volts obtained from the values of $(c + \bar{v} + \bar{W})$ and $(c + \bar{v}/2 + w)$, taking $\bar{W} = \bar{w}$:—

$X/p.$	$\bar{v}.$	$c + \bar{w}.$
5	15	21
10	17.6	14.4
16	18.6	12.9
30	25	10.0
47.5	31.8	9.5

12. The figures in the table confirm the obvious explanation of the phenomena indicated by the form and relative positions of the curves shown in fig. 1, or by the curve (fig. 3). Both methods of investigation lead independently to the conclusion that with a constant force X the loss of energy w increases with the pressure, and the average energy $(c + \bar{v})$ in the collisions which result in ionization increases as the pressure is reduced.

The figures in the column $(c + \bar{w})$ show that the energy c required to ionize a molecule of helium does not exceed 10 volts.

The smallest value of the energy $(\bar{v})$ is obtained with the smallest value of the ratio X/p . Since $\bar{v}$ represents an average energy, some molecules must be ionized in collisions where the energy of the electron is less than 25 volts. The curves (fig. 1) indicate that molecules are ionized in some cases when the energy $(c + \bar{v})$ of the electron is less than 22 volts.

It appears, therefore, that the kinetic energy of the electron must be at least twice the energy required to ionize a molecule in order that ionization may actually take place to an appreciable extent.

13. The results differ from the conclusions to which physicists have been led by applying the quantum theory to determine the transformations of energy which occur when electrons with comparatively small energy, of the order of 20 volts, collide with molecules. These conclusions are founded on the hypothesis that what may be a possible transformation of energy is, in fact, a transformation which is likely to occur in a large proportion of the total number of collisions in which the energy of the electron slightly exceeds a certain critical value. This theory has led to the conclusion that a large amount of energy is transferred from an electron to a molecule when the energy of the electron before the collision exceeds certain critical values V_1 , V_2 , &c. called resonance potentials. Having absorbed one of these quantities of energy, the molecule is then in a partially ionized state, or in a state in which it may emit radiation having a frequency proportional to V_1 or V_2 , &c. In addition there is the potential V_i , which is greater than the resonance potentials and represents the energy required to ionize a molecule. When the energy of an electron exceeds this value, it ionizes a molecule; but this conclusion is qualified by some supporters of the theory, who are of opinion that ionization may not occur in all cases when the energy of the electron exceeds the value V_i . The general impression is that molecules are ionized in a large proportion of such collisions.

Several experiments have been interpreted as supporting these conclusions; but the evidence is not very convincing, and various values have been found for the critical potentials. For example, some experiments have been interpreted as indicating that the ionization potential in helium is 29.3 volts, as given by Bohr's calculations; but the evidence of other experiments indicated that this potential is 20 volts. Many supporters of the theory state that this ionizing potential is 25 volts, and that the resonance potentials are between 20 and 25 volts for helium, so that we may adopt these numbers in considering the theory in connexion with the experiments we have described.

14. The most elementary experiments are those in which the initial effects of ionization by collision are investigated. When an electron starts from the negative electrode and moves under an electric force through the gas, it must make

several collisions with molecules when its energy is above the resonance potential V_1 before attaining the ionizing potential V_i . Whatever be the values of these potentials, the probability of losing energy in amounts corresponding to resonance potentials is greater than the probability of ionizing a molecule. The quantities of energy W and $\bar{w}$ lost in collision with molecules which are not ionized would therefore be comparable with the energy c lost in ionizing one molecule, and since the minimum value of $(c + \bar{w})$ is about 10 volts, the quantity c would under these circumstances be much less than 10 volts.

In cases where the pressure of the gas is high, as in some of the experiments represented by the curves (fig. 1) where the electrons make a large number of collisions with molecules, it has been suggested that the electrons never attain the energy corresponding to the ionization potential, but that molecules are ionized as a result of two collisions. Thus, when an electron with the energy 20 volts corresponding to one of the resonance potentials collides with a molecule, the molecule is partly ionized, and is completely ionized in another collision by an electron with an amount of energy corresponding to 5 volts. This may occur to an appreciable extent when the currents are large, but in these experiments the number N of electrons which pass through the gas from the negative to the positive electrode is so small that the number of molecules which could be ionized by this process is less than $N \times 10^{-6}$. Also, with small currents the number of molecules ionized by this process would be proportional to N^2 ; and as it has been found that the curves in figs. 1 and 3 are independent of the number N , the number of molecules which may be ionized as a result of two collisions must be inappreciable. The increase in conductivity which has been observed must therefore be attributed to ionization by single collisions.

With the pressures and forces used in these experiments, electrons make several collisions with molecules while moving with velocities less than that corresponding to 25 volts, but greater than the potentials corresponding to resonance. If they lost their energy in these collisions they never could attain their ionizing potential. The statements frequently made as to the loss of energy of electrons in amounts corresponding to resonance potentials are inconsistent with these experiments and similar experiments made with other gases.

It appears from this investigation that electrons moving with velocities corresponding to resonance potentials very rarely lose their energy when they collide with molecules.

XXXIII. *A Tentative Theory of the Capture and Loss of Electrons by Swift Nuclei.* By R. H. FOWLER, *Fellow and Lecturer in Mathematics in Trinity College, Cambridge* *.

§ 1. *INTRODUCTION.* *The experimental facts.*—The phenomena of capture and loss of electrons by swift α -particles, first detected by Henderson †, have recently been studied in some detail by Rutherford—his results have just been published ‡. He establishes that when a beam of α -particles of given velocity emerges from a thin foil, the beam is not homogeneous but consists in general of a mixture of He^{++} , He^+ and even He . The last named are only present to a noteworthy extent at the lowest velocities examinable by the scintillation method, and we shall not in general refer further to them in this paper. The emergent beam consists then of He^{++} and He^+ present in a definite ratio, which depends on the velocity of the α -particles. The ratio further does not depend to any marked extent on the material of the foil, though there is a perceptible tendency for the number of He^+ to be greater for gold foils than for foils of lighter elements. It is thus clearly established that the action of the thinnest foil is to set up a definite equilibrium ratio between He^{++} and He^+ in the beam, which is a rapidly varying function of the velocity of the beam and almost independent of all other conditions.

These phenomena are only observable with a very good vacuum in the deflecting chamber in which the beam is analysed by the usual strong magnetic field. The phenomena which occur when gas is admitted are very significant. The first effect is to wipe out altogether the He^+ particles, showing that they have lost their electron in a gas collision and have not in general picked one up again for an appreciable distance. A closer examination of the distribution of the scintillations shows, however, that at suitable gas pressures an appreciable number of both captures and losses do take place along the long path of the α -particle through the analysing chamber. This is established by the marked narrowing of the main band due to He^{++} . The slow over-deflected α -particles have an average charge of less than 2 when they have reasonable chances of capture, and therefore are less over-deflected when gas is admitted, relatively to the normal ones.

The ratio of the numbers of He^{++} to He^+ varies with the

* Communicated by the Author.

† Henderson, *Proc. Roy. Soc. A.* cii. p. 496 (1922).

‡ Rutherford, *supra*, p. 277.

velocity over a wide range as a power of the velocity somewhere between 4.6 and 5. This variation has been tested from about the velocity of the α -particle from RaC (1.922×10^9 cm./sec., or 1040 equivalent electron-volts) down to α -particles of about 1/10 this energy, say 100 volts. At the top velocity (more precisely 1080 volts obtained with α -particles from ThC) the numerical value of the ratio is about 330, falling to 1 at the lower. The precise figures will be discussed later.

The equilibrium concentration ratio $[\text{He}^{++}]/[\text{He}^+]$ in the beam is expressed by Rutherford in another form. He points out that if λ_c is the mean free path for capture and λ_l the mean free path for loss in the foil, then

$$[\text{He}^{++}]/[\text{He}^+] = \lambda_c/\lambda_l. \quad . \quad . \quad . \quad (1)$$

He then shows that since the ratio λ_c/λ_l is practically independent of the nature of the foil, it will probably be the same in the gas. In the gas λ_l can be determined absolutely by observing the gas pressure required to abolish the He^+ band. The actual value of λ_l , the free path for loss, is about that to be expected from our knowledge of the general process of ionization by collision and varies in the expected way with the velocity. The experiments thus determine absolutely both λ_c and λ_l . In the following sections we put forward a tentative theory of the action, which accounts roughly, even quantitatively for the observed facts.

§ 2. *A crude application of the theory of thermodynamic equilibrium.*—The nature of the equilibrium ratio established by Rutherford and its rough independence of almost everything except velocity suggests that this equilibrium ratio may conceivably represent roughly the ratio of the equilibrium concentrations of He^{++} and He^+ which would be observed in a suitable gaseous assembly in thermodynamic equilibrium. So far as the relative interaction of the α -particle and an atom or electron is concerned, only the relative motion is relevant. It makes no difference therefore to the relative orbits whether we consider the α -particle or the atom and its electrons in motion. Let us contemplate then fixed or nearly fixed α -particles bombarded by a stream of swift atoms. So far as the vast majority of such interactions are concerned the effect of the nucleus of the bombarding atom may not be serious, and the interaction with any or all of the lightly bound electrons in such an atom must clearly be very much the same as if they were a cloud of free electrons of the same density in space. We may suppose in this

connexion that an electron is "lightly bound" if the energy required to remove it from the atom is a fairly small fraction of its equivalent energy as a member of the swarm. We are thus led to suppose that as a first very crude approximation most of the interactions between the α -particle and the atoms of the foil which result in captures or losses will take place just as in a gaseous assembly at a temperature which makes the mean energy of an electron equal to that of an electron with the speed of an α -particle, and at an electron density which is that of the lightly bound electrons in the foil.

The dissociative equilibrium, $\text{He}^+ \rightleftharpoons \text{He}^{++} + \text{electron}$, is governed by well-known laws. If we may suppose that the He^+ can only exist with its electron in the final (normal) one-quantum orbit,—this will be examined more closely later on—then the equilibrium state is *

$$\frac{[\text{He}^{++}]\text{P}_e}{[\text{He}^+]} = \frac{0.332}{2} T^{5/2} e^{-\chi/kT}. \quad \dots (2)$$

In this equation χ is the ionization potential of normal He^+ (54 volts), P_e is the partial electron pressure, and k is Boltzmann's constant. To find the temperature T we have to equate $\frac{3}{2}kT$, expressed in volts, to W the speed of the α -particle in the same units. For this purpose we have

$$kT \text{ volts} = 8.60 \times 10^{-5} T, \quad (T \text{ in } ^\circ\text{C}).$$

Formula (2) refers to P_e , and we require ν_e the electron density which is given by

$$\text{P} = \nu_e kT. \quad \dots (3)$$

Thus we take for the equilibrium law

$$\begin{aligned} \frac{[\text{He}^{++}]\nu_e}{[\text{He}^+]} &= \frac{0.332}{2k} T^{3/2} e^{-\chi/kT}, \\ &= 8.25 \times 10^{20} W^{3/2} e^{-81/W}, \quad \dots (4) \end{aligned}$$

where W is the speed of the α -particle in volts. It is interesting to note that the temperature corresponding to 1040 volts is about 5,800,000° C.

Electron densities in foils can be fairly easily calculated. For Al the L-electrons are bound with about 70–80 volts †. We may probably take Al to have 11 electrons effectively

* See, for example, Fowler and Milne, Monthly Notices R. A. S. lxxxiii. pp. 407, 408 (1923).

† Here and elsewhere the data for the energy levels are taken from Bohr and Coster, *Zeits. f. Phys.* xii. p. 350 (1923).

free at all the higher speeds concerned, diminishing somewhat at the lower velocities. The density of the metal is 2.70 and the mass of an atom $27 \times 1.662 \times 10^{-24}$ gm. Thus

$$\nu_e(\text{Al}) = 6.6 \times 10^{23}.$$

For Ag the N- and O-level electrons, 19 in all, will be free at all the higher speeds; of these, 13 are bound with 45 volts or less, and 6 with about 100 volts. The M- (and other) level electrons which are bound with at least 370 volts, will be practically always permanently bound. Thus

$$\nu_e(\text{Ag}) = 1.11 \times 10^{24}$$

at the higher speeds, with much the same proportional diminution as for Al. For Au the electrons of the N_{VI} , N_{VII} , O-, and P-levels are similarly free, 27 in all, while the others are similarly bound. Thus

$$\nu_e(\text{Au}) = 1.59 \times 10^{24},$$

with similar variations. A substance like Cellulose $C_6H_{10}O_5$ seems to lead to an electron density about 4×10^{23} . Mica is difficult to calculate for exactly, but there is every reason to anticipate a result very little different from $\nu_e(\text{Al})$. The electron densities thus calculated are very uniform, showing merely a slight increase with atomic weight. If as a rough figure we accept $\nu_e = 6.6 \times 10^{23}$, we have

$$[\text{He}^{++}]/[\text{He}^+] = 1.25 \times 10^{-8} W^{3/2} e^{-81/W}, \quad (W \text{ volts}).$$

We arrive at once at

$$W = 1000, \quad [\text{He}^{++}]/[\text{He}^+] = 40,$$

$$W = 100, \quad [\text{He}^{++}]/[\text{He}^+] = 0.56.$$

The corresponding experimental figures are about 1 and 330. The agreement with this extremely rough calculation is amply sufficient to encourage us in thinking that we are discussing the phenomenon on the right lines and in attempting to better the theory by re-examining it with the help of some definite mechanism by which the captures and losses may be effected. In the light of the above agreement the mechanism may be supposed to be one which, in an ordinary assembly, will set up exactly the ordinary equilibrium laws.

One further salient point remains to be considered—that is that the ratio of the free paths for capture and loss seems to be the same in the foil and in a dilute gas. In the light of (2) no such state of affairs could possibly hold good if P_e or ν_e refer to the *general* electron pressure or density. We must suppose, and this is in agreement with all the

weight of other evidence, that the ν_e of the formula is the ν_e inside an atom or molecule, and that in any case of capture or loss the whole of the interaction is provided by the electrons (or perhaps electrons and nuclei) belonging to a single atom or molecule. The rest of space can as it were be wiped out; nothing whatever happens there. On this view, which seems in any case to be correct, our preceding calculations for foils will not be substantially affected, for the ν_e for atoms and the ν_e for metallic foils or mica slips are not greatly different. The former may be larger by a factor of 2 or 3. The calculations will thus apply at once to similar atoms in a gaseous as well as in a solid state.

§ 3. *Application of the theory of capture and loss by electronic collision in gaseous assemblies in statistical equilibrium.*—As a result of the foregoing considerations we must treat the $[\text{He}^{++}]/[\text{He}^+]$ equilibrium as equivalent to the thermodynamic or statistical equilibrium of a gaseous assembly at high temperature, modified by certain peculiar circumstances, of which obviously the most important is the fact that all the electrons have about the same velocity relative to the α -particles instead of velocities distributed according to Maxwell's Law. We are going to use as an analogy to the process of capture and loss by flying α -particles the ordinary processes of capture and loss which certainly govern the state of an assembly in genuine dissociative equilibrium. To apply the laws of such processes to this distorted case we must have a knowledge of these laws in certain detail. This knowledge of detail is available to a sufficient extent to make a start on the problem of the α -particle.

In an ordinary assembly captures and losses can take place by two main mechanisms—radiative or non-radiative—the latter in the simplest case are collisions in which at one stage or another three bodies are concerned—for example, an He nucleus and two electrons. We shall consider at a later stage the evidence that leads one to believe that the processes of capture and loss of electrons by α -particles are essentially non-radiative. It is possible to work out the laws of capture and loss by the simplest collisions in exactly the same way as Klein and Rosseland* have worked out the laws of collisions of the first and second kind†. The process of loss is merely ionization by electronic impact. It is there shown that the associated reverse process must be assumed

* Klein and Rosseland, *Zeits. f. Phys.* iv. p. 46 (1921).

† Fowler, *supra*, p. 257.

to be a three-body collision in which one electron is bound by the atom, and the other goes off with all the superfluous energy. The number of a definite type of ionizations by collision per cubic centimetre per second may be written

$$x_1 \left(\frac{2\epsilon}{m} \right)^{1/2} \mu(\epsilon) d\epsilon S_1^2(\eta, \epsilon) d\eta : \dots (5)$$

this is the number due to electrons with energy between ϵ and $\epsilon + d\epsilon$ (ϵ -electrons), which results in knocking out an η -electron. If ϵ_0 is the ionization potential $S_1^2(\eta, \epsilon) \equiv 0$, when $\epsilon < \epsilon_0 + \eta$. The number of captures per cubic centimetre per second in which a ξ -electron is bound by the interaction of a ξ -electron is similarly

$$x_2 \left(\frac{2\xi}{m} \right)^{1/2} \mu(\xi) d\xi \left(\frac{2\xi}{m} \right)^{1/2} \mu(\xi) d\xi S_2^1(\xi, \xi). \dots (6)$$

Here x_1 and x_2 are the concentrations of atoms and ions (or He^+ and He^{++}) respectively and $\mu(\xi)d\xi$ is Maxwell's distribution law for electrons. To preserve the usual laws of statistical equilibrium it is further shown that we must have for all α and η

$$(\epsilon_0 + \eta + \alpha) S_1^2(\eta, \epsilon_0 + \eta + \alpha) = \frac{8\pi m \sigma}{q h^3} \alpha \eta S_2^1(\eta, \alpha). \dots (7)$$

In equation (7) and elsewhere m is the mass of the electron, σ is the number of equivalent electrons removable with expenditure of work ϵ_0 , q is the "weight" of the atom in its normal state relative to the ion, and h is Planck's constant.

It is further shown on the basis of the classical ionization theory of J. J. Thomson that

$$S_1^2(\eta, \epsilon) = \frac{A \sigma}{\epsilon} \frac{1}{(\eta + \epsilon_0)^2} \dots (8)$$

and therefore that

$$S_2^1(\eta, \alpha) = \frac{1}{\alpha \eta} \frac{q h^3}{8 \pi m} \frac{A}{(\eta + \epsilon_0)^2} \dots (9)$$

Equation (8) is substantially equivalent to the V^4 -law for the ranges of β -particles, expressed in the present notation. It may be thought of here as fully equivalent to this law and of the same range of validity. Since we are concerned with only moderate velocities and fundamentally with only electron-electron interactions we do not require the relativistic modifications.

On the strict classical theory $A = \pi e^4$. This value may be

too small by a factor of perhaps 2 or 3, but the exact value of A (provided it is constant) is only of secondary importance here.

If ionization by electronic impact and the associated reverse process form the mechanism which controls the equilibrium $[\text{He}^{++}]/[\text{He}^+]$ in the beam of α -particles, it is easy to deduce a much more precise theoretical value for this ratio on the basis of (6) and (7). As a first approximation we may suppose that all the electrons have an energy W , so that the electron distribution law here, instead of Maxwell's law, is

$$\begin{aligned}\mu(\epsilon)d\epsilon &= \nu_e, & (\epsilon=W), \\ \mu(\epsilon)d\epsilon &= 0, & (\epsilon \neq W).\end{aligned}$$

The rate of production of He^{++} by ionization is therefore by (5) and (8)

$$[\text{He}^+] \left(\frac{2W}{m} \right)^{1/2} \nu_e \int_0^{W-\epsilon_0} \frac{A\sigma}{W(\eta+\epsilon_0)^2} d\eta$$

or

$$[\text{He}^+] \nu_e \left(\frac{2}{mW} \right)^{1/2} A\sigma \left(\frac{1}{\epsilon_0} - \frac{1}{W} \right). \quad (10)$$

The rate of production of He^+ by capture is by (6) and (9).

$$[\text{He}^{++}] \nu_e^2 \frac{2}{mW} \frac{qh^3}{8\pi m} \frac{A}{(W+\epsilon_0)^2}. \quad (11)$$

The equilibrium ratio must therefore be given by the equation

$$\frac{[\text{He}^{++}]}{[\text{He}^+]} \nu_e = \frac{8\pi m\sigma}{qh^3} \left(\frac{m}{2} \right)^{1/2} \frac{W-\epsilon_0}{W\epsilon_0} W^{1/2} (W+\epsilon_0)^2. \quad (12)$$

We observe at once that for values of W fairly large compared with ϵ_0 (54 volts) equation (12) predicts a variation

$$[\text{He}^{++}]/[\text{He}^+] \propto W^{5/2} \propto V^5, \quad (13)$$

which is in substantial agreement with Rutherford's observations ($V^{4.6}$ or V^5). What is more, the actual numerical agreement is far better than could have been hoped. If we express all the energies in (12) in volts (1 volt = 1.591×10^{-12} erg) and insert the usual numerical values $m = 9.00 \times 10^{-28}$, $h = 6.55 \times 10^{-27}$ and the values proper to He^+ , $q=2$, $\sigma=1$, we find that

$$\frac{[\text{He}^{++}]}{[\text{He}^+]} \nu_e = 1.71 \times 10^{21} \frac{W-\epsilon_0}{W\epsilon_0} W^{1/2} (W+\epsilon_0)^2, \quad (W, \epsilon_0, \text{volts}). \quad (13)'$$

If we take as a round figure $v_e = 10^{24}$, we obtain the following table for comparison with Rutherford's experimental values.

TABLE I.

W Volts.	$[\text{He}^{++}]/[\text{He}^+]$ Calc. $v_e = 10^{24}$.	$[\text{He}^{++}]/[\text{He}^+]$ Obs.	$[\text{He}^{++}]/[\text{He}^+]$ Calc. $v_e = 4 \times 10^{24}$.
1080	1270	330	320
920	860	200	215
600	300	67	75
230	30	7.5	7.5
100	3.5	1.0	{ 0.9
90	2.6		{ 0.65

The table shows that an excellent agreement between theory and experiment could be obtained if we were at liberty to suppose that v_e had values of the order $3, 4 \times 10^{24}$ for all velocities. These values are perhaps slightly high, particularly for low velocities. But they are probably to be modified in a downward sense in view of certain other considerations in the next section. The general conclusions would seem to be favourable to the theory.

§4. *A critical examination of the assumptions of the theory.*—

It is well to pause at this stage and reconsider the basis of these results. We have assumed

(i.) That captures and losses take place inside an individual atom or molecule much as if the lightly-bound electrons were a free electron gas of equivalent density.

(ii.) That the mechanism of capture and loss is the ordinary mechanism of ionization by electronic impact together with the associated reverse process of radiationless three-body capture.

(iii.) That the part played by the core of the atom (nucleus + tightly-bound electrons) may be ignored.

(iv.) That in the case of He^+ only the normal 1-quantum orbit is effectively present under the given conditions.

We have little or no reason to question the applicability of (i.) at the higher velocities. It is substantiated by any theory of ionization by α - and β -particles.

Under (ii.) we should notice that the coefficients S_1^2 and S_2^1 refer strictly to the conditions of gaseous assemblies in

which the electron velocities are distributed in all directions and are not almost unidirectional as here. Thus the S_1^2 and S_2^2 which we have used are really averages taken over all relative orientations of the axis of the atom, and the directions of motions of any incident electron or electrons. The unidirectional bombardment here may very well not affect S_1^2 , but on the other hand it may equally well seriously affect S_2^2 . If the capture process is really the reverse of the ionization process in every detail, the most effective relative direction of incidence for capture may well be nearly at right angles, since the electrons after ionization has occurred will in general be moving more or less at right angles. This effect should cut down captures and still further increase the ratio $[\text{He}^{++}]/[\text{He}^+]$ at high velocities, but by how much it would be far from easy to calculate.

In the same connexion we may point out that there is no need to make the stringent assumption that all the bombarding stream have velocities exactly equivalent to W volts. It is easy to allow for a combination of this with another velocity orientated in a random direction; this will represent approximately the motion of the electrons in the atom. For this purpose one must work primarily in velocities rather than energies. One then finds that if the velocity of the electron stream is V , and the orbital velocities v , then

$$\mu(\epsilon)d\epsilon = \frac{\nu_e}{2v} \frac{1}{(2m)^{1/2}} \frac{d\epsilon}{\sqrt{\epsilon}}, \quad (\tfrac{1}{2}m(V-v)^2 < \epsilon < \tfrac{1}{2}m(V+v)^2),$$

$$= 0, \quad (\epsilon > \tfrac{1}{2}m(V+v)^2, \epsilon < \tfrac{1}{2}m(V-v)^2).$$

The resulting integrals are still of simple forms and easily evaluated. One finds that ionizations now occur at a rate

$$[\text{He}^+] \nu_e \frac{A\sigma}{m} \frac{1}{v} \left[\frac{1}{\epsilon_0} \log \frac{V+v}{V-v} - \frac{4Vv}{m(V^2-v^2)^2} \right],$$

provided that $\tfrac{1}{2}m(V-v)^2 > \epsilon_0$, and captures at a rate

$$[\text{He}^{++}] \nu_e^2 \frac{A}{m^2} \frac{qh^3}{8\pi m} \frac{1}{2v^2} \log \frac{V+v}{V-v} \cdot \left[\frac{2}{\epsilon_0^2} \log \frac{V+v}{V-v} \right. \\ \left. - \frac{1}{\epsilon_0^2} \log \frac{\tfrac{1}{2}m(V+v)^2 + \epsilon_0}{\tfrac{1}{2}m(V-v)^2 + \epsilon_0} - \frac{1}{\epsilon_0} \left\{ \frac{1}{\tfrac{1}{2}m(V-v)^2 + \epsilon_0} \right. \right. \\ \left. \left. - \frac{1}{\tfrac{1}{2}m(V+v)^2 + \epsilon_0} \right\} \right].$$

The modified form for the rate of loss for $\tfrac{1}{2}m(V-v)^2 < \epsilon_0$ can easily be obtained when required. The formulæ are a

little complicated and numerical values must be inserted to estimate the effect. Taking the voltages corresponding to v and ϵ_0 as 25 and 50, and to V the values 900, 225, and 100, we find that the calculated values of $[\text{He}^{++}]/[\text{He}^+]$ are smaller by the factors 1/1.13, 1/1.58, and 1/2.8. These corrections have the effect of diminishing the v_e necessary for agreement in Table I., and are of just the right nature to allow for a reasonable decrease in effective v_e with decreasing velocity. One can scarcely push the correction further at this stage.

With reference to (iii.) we may observe that the neglect of the core is certainly not justifiable *a priori*. It should be possible to take account of it in just the same way as we have taken account of the "free" electrons on the basis of a mechanism of ionization and its reverse capture by means of collisions in which a heavily charged core knocks out electrons or helps to bind them in another atom. This requires, however, a knowledge of the relation analogous to (7) for the case in which two of the bodies are of comparable mass, which has not yet been worked out. We may observe, however, that we must expect to obtain relations of the same general type as (7), (8), and (9). The classical theory of the production of primary ionization by α -particles for example indicates a value for the new $S_1^2(\eta, \epsilon)$ closely analogous to (8). It is therefore very probable that even if the effect of the core is sufficient seriously to influence the individual rates of capture and loss, their ratio will be affected only to a secondary extent.

It must be pointed out that assumption (iv.) is open to question, although physically it would seem eminently reasonable. The arguments of statistical mechanics are based on the assumption of "limited interferences"—that is that any particular state of any atom or other system in general exists undisturbed in the assembly for times which are long compared with the times during which energy exchanges are taking place. All states for which this condition is fulfilled must be included, but it is not yet possible to say for certain where the line is to be drawn to exclude states other than these. An indication can, however, be obtained by considering how often on the average per revolution the electron will be removed from an orbit in He^+ by electrons of velocity W and space density 10^{24} . The number of ionizations per atom per second is then

$$v_e \left(\frac{2}{mW} \right)^{1/2} A \left(\frac{1}{\epsilon_0} - \frac{1}{W} \right), \quad \quad (14)$$

which works out at about 2.2×10^{15} per sec. for the normal

1-quantum orbit and $W=1000$. The orbital frequency for this orbit is 2.6×10^{16} as calculated from the ordinary formulæ. There is thus on the average one removal for every ten revolutions, which is a reasonably small amount of disturbance. But for an n -quantum orbit the ionization frequency is multiplied by n^2 and the orbital frequency by $1/n^3$. Thus the n -quantum orbit will exist undisturbed on the average for only $10/n^5$ revolutions. The 2-quantum orbit can exist on the average only for $\frac{1}{8}$ of a revolution, and every other orbit for a much smaller fraction. It is possible that we should think of the 2-quantum orbit (of weight 6) as being effective or partially effective. We can hardly expect any other orbits of higher quantum number than 2. This point of view is supported by the relative sizes of the orbits. The radius of the 1-quantum orbit is 2.6×10^{-9} cm., of the 2-quantum orbit 1.06×10^{-8} cm. The average distance apart of electrons at a density 10^{24} is about 10^{-8} cm.

What follows is exceedingly speculative, but perhaps suggestive. If in the corresponding assembly in statistical equilibrium He^+ in the 2-quantum orbit is to any degree effectively present, we must suppose it present here to the corresponding extent. Relations for capture and loss to and from the 2-quantum state will be formally the same as for the 1-quantum state with new values of q and ϵ_0 . We obtain at once the analogue of (12),

$$\frac{[\text{He}^{++}] \nu}{[\text{He}^+]_2} = \frac{8\pi m \sigma (m)^{1/2} W - (\epsilon_0)_2 W^{1/2}}{q_2 h^3 (2)} (W + (\epsilon_0)_2)^2, \quad (15)$$

in which the suffix 2 denotes the 2-quantum state of the atom. Since $q_2=6$, $(\epsilon_0)_2 = \frac{1}{4}\epsilon_0$ we find very approximately from (12) and (15) that

$$\frac{[\text{He}^{++}] \nu_e}{[\text{He}^+] + [\text{He}^+]_2} = \frac{[\text{He}^{++}] \nu_e}{[\text{He}^+]} \times \frac{2}{2+1.5}.$$

It is just possible that some part of the numerical discrepancy in Table I. may be properly and simply accounted for in this way. Further speculation, however, on these lines is hardly profitable at this stage, and we shall not assume any appreciable fraction of captures into a two or more quantum orbit in the rest of the discussion here.

§ 5. *The mean free path for loss, λ_l .*—The rate of loss of electrons per atom per second by the $[\text{He}^+]$ is given by (14). We derive the mean free path for loss λ_l by dividing the

velocity $(2W/m)^{1/2}$ by the expression (14). Thus

$$\lambda_i = \frac{W}{\nu_e A \left(\frac{1}{\epsilon_0} - \frac{1}{W} \right)} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Thus makes $\lambda_i \propto V^2$, a law which is probably not exactly correct; Rutherford's experiments seem to make λ_i vary more nearly as V over the range $0.94V_0$, $0.47V_0$, where V_0 is the initial velocity of the α -particle from RaC . But this deviation is of course just the deviation from experimental fact inherent in all current theories of the ionization due to α -particles, and is not unexpected here. In (16) ν_e refers strictly to atomic interiors—no collisions of any sort occurring outside. To find, however, the numerical value of λ_i in air, say, we need only interpret ν_e in (16) as the ν_e of the air. It makes no difference to the average number of collisions leading to loss if the electrons causing the loss are distributed in dense clouds (atoms) or uniformly, provided the average electron density is the same. The resulting value of ν_e may be taken to be $10.4 \times 2.70 \times 10^{19}$ per cubic centimetre for air at normal pressure and temperature. The average number of loosely bound electrons in the air molecule is 10.4. We thus find

$$\lambda_i = 3.47 \times 10^{-8} \frac{W^2 \epsilon_0}{W - \epsilon_0} \quad (W, \epsilon_0, \text{ volts}) \quad . \quad (17)$$

The observed and calculated values of λ_i are given in Table II.

TABLE II.

Velocity in terms of V_0 .	Velocity in volts.	λ_i obs. mm.	λ_i calc. mm.
0.94	920	0.011	0.019
0.76	600	0.0078	0.013
0.47	230	0.0050	0.0058

The agreement is very satisfactory. In this calculation there is no possible doubt as to ν_e . One would perhaps have expected the calculated λ_i to exceed the observed λ_i by a somewhat greater factor than it does, as there is the effect of the hard core to be allowed for. But we may rest content with Table II. at this stage.

§ 6. *The equilibrium ratio $[H^+]/[H]$ in a beam of positive rays.*—It has recently been shown by Rüchardt *, in some very convincing experiments, that in a beam of hydrogen positive rays travelling through various gases a definite equilibrium ratio $[H^+]/[H]$ is set up, which varies rapidly with the velocity. The H^+ particles had been accelerated by fields varying from 36,000 to 16,000 volts, so that their equivalent velocities are only from 19.5 to 8.5 volts, and are very low for the applicability of the present method. For the highest velocities the theory should still perhaps be roughly applicable. Rüchardt gives the following values :

$$\begin{aligned}[H^+]/[H] &= 0.51 \text{ at } 19.5 \text{ volts in } H_2, \\ &= 0.89 \text{ at } 18.7 \text{ volts in } N_2, \\ &= 1.02 \text{ at } 19.8 \text{ volts in } O_2.\end{aligned}$$

We have to apply formula (13)', the only difference being that now $\epsilon_0 = 13.54$ volts. We thus obtain

$$\begin{aligned}[H^+]\nu_e/[H] &= 1.9 \times 10^{23} \text{ at } 19.5 \text{ volts,} \\ &= 1.6 \times 10^{23} \text{ at } 18.7 \text{ volts,} \\ &= 2.0 \times 10^{23} \text{ at } 19.8 \text{ volts.}\end{aligned}$$

The ratios will agree at the top velocities with Rüchardt's observations if we have molecular electron densities

$$\begin{aligned}\nu_e &= 3.7 \times 10^{23} \text{ in } H_2, \\ \nu_e &= 1.8 \times 10^{23} \text{ in } N_2, \\ \nu_e &= 2.0 \times 10^{23} \text{ in } O_2.\end{aligned}$$

Since only the most lightly-bound electrons can be concerned (17 volts at the very most) these figures are not inconsistent among themselves and are not inconsistent with a value of $\nu_e = 10^{24}$ for higher velocities. At the same time we have obviously already strained the theory to the breaking point in applying it to these very low velocities. That agreement still persists to this extent is eminently satisfactory. We may observe finally that the V^5 -law still seems to persist in this region for the observations in H_2 and O_2 . The observations in N_2 are hardly consistent, for they show a quite different and much slower variation.

§ 7. *General Discussion.*—The foregoing considerations, incomplete as they unfortunately are, seem to indicate that

the controlling mechanism by which the equilibrium ratio is set up in the beam of α -particles is a mechanism of loss and capture by collision processes of a definite type. In arriving at this conclusion we have found it desirable to consider the α -particles as at rest and the electrons as in motion with the appropriate velocity. This is of course legitimate here, for it is only the relative motion that affects the processes of capture or loss which can be referred directly to the circumstances of the relative orbit. It is of course equally true that the actual exchanges of energy between the particles depend on the absolute velocities, not merely on the relative velocity. This must be borne in mind in forming a detailed physical picture of the action of these mechanisms.

We have not here discussed the possibility of a radiative mechanism of capture. It appears to me however, that, as far as this can be discussed at present, it leads to a wrong variation with velocity. The number of captures per He^{++} per second varies here as $1/V^6$, the mean free path for capture as V^7 . It appears that Kramer's* calculations lead to a chance of capture by radiation in any single encounter which varies as $1/V^4$. The captures per He^{++} per second by this mechanism vary therefore as $1/V^3$ and the free path as V^4 . In view of this discrepancy I have not used Kramer's results to calculate the absolute rate of capture by radiation at any velocity. The experimental facts on velocity variation are sufficient to establish that radiative captures play only a subordinate part.

It is perhaps here permissible to stress certain points suggested by the theory as likely to repay further investigation. The quantity ν_e , the intra-atomic "free" electron density, plays a fundamental part in the theory. If the theory is in any way correct the equilibrium ratio $[\text{He}^{++}]/[\text{He}^+]$ ought to vary from foil to foil like $1/\nu_e$. We can be fairly certain *a priori* of the relative values of ν_e for different atoms for a given velocity. A detailed experimental investigation of this variation at a number of velocities would provide a fairly crucial test of the theory. It would further prove of great interest to examine, if it is possible, the equilibrium ratio for swift H^+ - and H -particles; one would thus extend R  chardt's investigations to a range of velocities of H -particles only attainable by collision with α -particles, at which the theory and observations are more directly comparable. One should thus be able to test with more

* Kramers, Phil. Mag. xlv. p. 836 (1923).

certainly the predicted variation of the equilibrium ratio with ϵ_0 . From the general theoretical point of view every possible examination of the theory is of the greatest interest. For the theory itself is of the nature of an extrapolation of statistical arguments to the conditions holding in an assembly at some $5,800,000^\circ \text{C}$. Gaseous assemblies such as these most certainly exist—the interiors of giant stars for example may be at even greater temperatures. To these we may hope to apply all the statistical ideas which have been and are now being developed. But any direct check on the theory, such as is provided by the present experiments, is of the greatest value in guaranteeing that our extrapolations of statistical mechanics to such assemblies have not, in some unexpected way, exceeded the range of validity.

§ 8. *Summary.*—The equilibrium ratio of the concentrations of He^{++} and He^+ in a beam of α -particles of given velocity is discussed in the light of Sir E. Rutherford's experiments.

It is shown that the equilibrium is probably of the nature of a thermodynamic equilibrium corresponding to an electron density equal to that of the lightly bound electrons in the interior of an atom [perhaps 2×10^{24} per c.c.] and a temperature equal to that at which electrons have on the average the velocity of the α -particle [$5,800,000^\circ \text{C}$. for the initial velocity of α -particles from RaC].

The mechanism of capture and loss is probably a collision-mechanism (non-radiative). Loss corresponds to ionization by electronic impact—capture to the strict reverse of this, a three-body collision. The ratio of the frequencies of such processes has been recently established by the author as an extension of the ideas of Klein and Rosseland. This ratio leads at once roughly to the observed equilibrium when it is applied to the conditions of the experiments on α -particles.

In conclusion it is a pleasure to thank Sir E. Rutherford for information supplied in advance of publication, and for many valuable critical discussions at all stages of the development of the theory.

XXXIV. *On a proposed Empirical Equation of State for Fluids.* By S. LEES, M.A., St. John's College, Cambridge*.

Introduction.

§ 1. **M**ANY investigators have devoted attention to the problem of framing an adequate equation of state for fluids in general. (By equation of state is meant a relation which must always be satisfied between the pressure p , volume V , and absolute temperature T for unit mass of a fluid.) Reference may here be made to the equations of van der Waals †, Clausius †, Dieterici †, Porter ‡, and others. Whilst there are objections on individual points to all of these equations, each of them has had success in certain directions in helping to rationalize the behaviour of gases and vapours.

In addition to the above-mentioned equations, which have some application for all values of the variables p , V , and T , reference may be made to others (*e.g.*, that of Callendar for steam, and that of D. Berthelot § for low pressures) which are intended to have but a restricted field or range of application for the variables. Such restricted equations of state have been extremely useful in compiling tables of properties of particular fluids for technical purposes.

In the following paper the author endeavours to develop an equation of the unrestrained type, and some apology may seem to be required for adding another to the existing equations of this type. The author is of opinion, however, that the equation he has to propose is simple in form, and of interest as agreeing on certain points more closely with experimental facts than other proposed (simple) formulæ. It is not claimed that the proposed equation has important esoteric significance. The method, in fact, which has been followed in connexion with this paper may be described as "formula-fitting," with a fairly frequent comparison with the experimental facts.

* Communicated by the Author.

† General reference may be made to Kuenen, *Die Zustandsgleichung der Gase und Flüssigkeiten*; also to H. Kamerlingh Onnes and W. H. Keesom, *Die Zustandsgleichung* (Art. v.10, *Encyklopädie der Math. Wissenschaften*; reprinted in *Communications from the Physical Laboratory of Leiden*).

‡ *Phil. Mag.* xliv. p. 1020 (1922).

§ *Trav. et Mém. du Bur. Internat.* xiii. (1907).

Type of Equation of State chosen.

§ 2. In building up an equation of state, certain assumptions are made in this paper. There is, firstly, the assumption that at high temperatures and low pressures, *i. e.* with large specific volumes V , the equation approaches asymptotically the perfect gas equation

$$pV = RT, \quad (1)$$

where R is the gas constant for unit mass. When this condition is satisfied, the fluid is sometimes said to be in the Avogadro-state. Secondly, it is assumed that at large pressures and low temperatures the volume V tends to a limit b which is to all intents and purposes identical with the volume of the fluid in the liquid condition.

Guided by these assumptions, the general type of equation of state has been taken as*

$$[p + \phi(p, V, T)] \cdot (V - b) = RT, \quad . . . (2)$$

where $\phi(p, V, T)$ is a function to be investigated and if possible to be determined. It may be noted that ϕ (by assumption) must tend to zero as V is made indefinitely large. It must also be such as not to interfere with the validity of the second of the above assumptions.

Critical Phenomena.

§ 3. A further and most important restriction on ϕ is that it must allow of the existence of critical phenomena. Assuming that this is the case, we shall have at the critical point

$$\left(\frac{\partial p}{\partial V}\right)_T = 0, \quad (3)$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0. (4)$$

From (2) we have

$$p = \frac{RT}{V - b} - \phi(p, V, T),$$

* The novel feature of this equation lies in making ϕ a function of the three variables p , V , and T . The usual theoretical interpretation of the factor $(V - b)$ would be that the volumes of the molecules (taken as proportional to b) are invariable.

and hence *

$$\left(\frac{\partial p}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} - \frac{\partial \phi}{\partial V} - \frac{\partial \phi}{\partial p} \left(\frac{\partial p}{\partial V}\right)_T,$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{\partial^2 \phi}{\partial V^2} - \frac{2\partial^2 \phi}{\partial p \partial V} \left(\frac{\partial p}{\partial V}\right)_T - \frac{\partial \phi}{\partial p} \left(\frac{\partial^2 p}{\partial V^2}\right)_T.$$

Equations (3) and (4) thus reduce to the simple results for the critical point

$$\frac{\partial \phi}{\partial V} = \frac{-RT}{(V-b)^2}, \quad \dots \quad (5)$$

$$\frac{\partial^2 \phi}{\partial V^2} = \frac{+2RT}{(V-b)^3}, \quad \dots \quad (6)$$

which, it will be noticed, do not at all involve explicitly the dependence of ϕ on p or T .

We now make the additional assumption † that $\phi(p, V, T)$ can be expressed as $\frac{1}{V^n} \psi(p, T)$, where n presumably will be positive to preserve the first of the assumptions of § 2.

In this case, we have $\partial \phi / \partial V = -n\psi / V^{n+1}$, $\partial^2 \phi / \partial V^2 = n(n+1)\psi / V^{n+2}$. Substituting these values in (5) and (6), and dividing the latter of these by the former, we obtain

$$\frac{n+1}{V} = \frac{2}{V-b},$$

$$\text{i. e.} \quad V_c = (n+1)b / (n-1). \quad \dots \quad (7)$$

The suffix c has been attached to V in (7) to indicate that we are referring solely to the critical volume.

In applying this result to determine n , it is assumed that the correct experimentally determined mean value of V_c is $4b$. This would appear to be very nearly the case ‡. In passing, it may be noted that van der Waals' equation makes $V_c = 3b$, whilst the equation of Dieterici gives $V_c = 2b$.

Substituting then $V_c = 4b$ in (7), we find $n = 5/3$. This

* In the differential coefficients of ϕ , only the independent variables indicated are supposed to vary. This is the usual notation.

† By using here a single power of V , and later in §§ 4 and 5 single powers of p and T respectively, we are assured of the equation of state satisfying the principle of corresponding states (see § 6).

‡ See, e. g., Lewis, 'System of Physical Chemistry,' 1918, vol. i. p. 80. *Phil. Mag.* S. 6, Vol. 47. No. 278. Feb. 1924. 2 F

may be compared with the value $n=2$ used in van der Waals' equation.

The obtained value of $n (=5/3)$ is supported in the strongest manner by the consideration of the ratio of $RT_c/p_c V_c$. We find from (5)

$$RT_c = n\psi_c(V_c - b)^2/V_c^{n+1}. \quad (8)$$

If this be used to eliminate ψ_c in

$$p_c = \frac{RT_c}{V_c - b} - \frac{\psi_c}{V_c^n},$$

we find

$$p_c = \frac{RT_c}{(V_c - b)^2} \left[V_c \left(1 - \frac{1}{n} \right) - b \right]. \quad (9)$$

If, as before, we assume $V_c = 4b$, we find $p_c = RT_c(3 - 4/n)/9b$. Hence

$$\frac{RT_c}{p_c V_c} = \frac{RT_c}{4bp_c} = 9/4(3 - 4/n). \quad (10)$$

We shall take the experimentally determined mean value of this ratio * to be $15/4$. In this connexion, it may be noted that whilst Dieterici's equation gives for this ratio about $3.7/1$, the equation of van der Waals gives for the ratio $8/3$.

Substituting $15/4$ for $RT_c/p_c V_c$ in (10), we find $n=5/3$ as before. This seems a remarkable result †.

We may sum up the results of this section by stating that if the equation

$$\left[p + \frac{\psi(p, T)}{V^{5/3}} \right] (V - b) = RT, \quad (11)$$

where $\psi(p, T)$ is as yet undetermined, gives a critical point, then at this critical point $V_c = 4b$, and $RT_c/p_c V_c = 15/4$; both of which results are in good agreement with experiments on a large number of gases.

Variation of the product pV .

§ 4. We proceed to discuss the variation of the product pV along an isothermal $T = \text{constant}$.

If we write (11) in the form

$$p = \frac{RT}{V - b} - \frac{\psi}{V^{5/3}}, \quad (11a)$$

* See Lewis, *loc. cit.* p. 79.

† An alternative procedure for this section is to assume

$$\phi = \psi(p, T)/(V - c)^n,$$

where c is a constant. We then find $c=0$ and $n=5/3$ as before.

we get on differentiation with respect to V (keeping T constant)

$$\left(\frac{\partial p}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{5\psi}{3V^{5/3}} - \frac{1}{V^{5/3}} \frac{\partial \psi}{\partial p} \left(\frac{\partial p}{\partial V}\right)_T,$$

$$\text{i. e. } \left(\frac{\partial p}{\partial V}\right)_T = \left[\frac{-RT}{(V-b)^2} + \frac{5\psi}{3V^{5/3}} \right] / \left[1 + \frac{\partial \psi}{\partial p} / V^{5/3} \right]. \quad (12)$$

Multiplying the right-hand side of (11a) by V to get the value of pV , we find on differentiation with respect to V along $T = \text{constant}$

$$\left[\frac{\partial(pV)}{\partial V} \right]_T = \frac{-bRT}{(V-b)^2} + \frac{2\psi}{3V^{5/3}} - \frac{1}{V^{2/3}} \frac{\partial \psi}{\partial p} \left(\frac{\partial p}{\partial V}\right)_T$$

$$= \frac{-bRT}{(V-b)^2} + \frac{2\psi}{3V^{5/3}}$$

$$- \frac{1}{V^{2/3}} \frac{\partial \psi}{\partial p} \left[\frac{-RT}{(V-b)^2} + \frac{5\psi}{3V^{5/3}} \right] / \left[1 + \frac{\partial \psi}{\partial p} / V^{5/3} \right]. \quad (13)$$

from (12).

Hence if pV has a minimum or stationary value on the isothermal, i. e. if $[\partial(pV)/\partial V]_T = 0$, then

$$\left[\frac{2\psi}{3V^{5/3}} - \frac{bRT}{(V-b)^2} \right] \left[1 + \frac{\partial \psi}{\partial p} / V^{5/3} \right]$$

$$= \frac{1}{V^{2/3}} \frac{\partial \psi}{\partial p} \left[\frac{-RT}{(V-b)^2} + \frac{5\psi}{3V^{5/3}} \right],$$

which reduces to

$$\frac{2\psi}{3V^{5/3}} - \frac{bRT}{(V-b)^2} - \frac{\psi}{V^{10/3}} \frac{\partial \psi}{\partial p} + \frac{RT}{(V-b)V^{5/3}} \frac{\partial \psi}{\partial p} = 0. \quad (14)$$

If T be supposed to be eliminated between (11a) and (14) we get the state path for the p, V diagram on which lie all minimum values of pV for the different isothermals. In general, the limiting value of pV on this path as V is made indefinitely great, i. e. p indefinitely small, need not be finite. But experiment goes to show* that a finite limiting value of pV under these circumstances does exist, and this fact may be made use of to specify ψ more closely. We make the further assumption that $\psi = p^\lambda f(T)$, where λ is to be found, and $f(T)$ is as yet arbitrary.

Under these circumstances, the relation (14), as V is made

* See, e. g., Lewis, *loc. cit.* p. 82.

indefinitely great for a fixed value of T , approaches asymptotically the relation

$$\frac{2}{3b} p^\lambda V^{1/3} f(T) - RT - \frac{\lambda p^{2\lambda-1}}{b V^{4/3}} [f(T)]^2 + \frac{\lambda RT}{b V^{2/3}} p^{\lambda-1} f(T) = 0, \quad (15)$$

i. e. approaches *

$$\frac{2}{3} \frac{(pV)^\lambda f(T)}{b V^{\lambda-1/3}} - RT - \frac{\lambda (pV)^{2\lambda-1} [f(T)]^2}{b V^{2\lambda+1/3}} + \frac{\lambda RT (pV)^{\lambda-1} f(T)}{b V^{\lambda-1/3}} = 0. \quad (15a)$$

Since pV is supposed finite under these conditions, we deduce that $\lambda = 1/3$, and further that

$$f(T) = 6RT \left/ \left[\frac{2}{3} (pV)^{1/3} + \frac{RT}{3(pV)^{2/3}} \right] \right. = b(RT)^{2/3}, \quad (16)$$

under the assumed conditions, viz., $pV \rightarrow RT$.

We may sum up the conclusions of this section by saying that if $\psi(p, T)$ of (11) involves a single power only of p , then considerations of the limiting value of the isothermal pV minima as $V \rightarrow \infty$ indicate that the equation of state is of the form

$$\left[p + \frac{p^{1/3} f(T)}{V^{5/3}} \right] (V - b) = RT. \quad (17)$$

The Nature of $f(T)$.

§ 5. We now assume $f(T)$ to be of the form aT^μ , where a and μ are constants, so that $\psi = ap^{1/3}T^\mu$.

From (8) and (9), remembering that $V = 4b$ and $n = 5/3$, we have respectively

$$RT_c = \frac{15}{4^{5/3}} \frac{ap_c^{1/3} T_c^\mu}{b^{2/3}}, \quad p_c = RT_c / 15b. \quad (18)$$

Hence, eliminating p_c , we find

$$R^{2/3} T_c^{2/3-\mu} = \frac{15^{2/3} a}{4^{8/3} b}. \quad (18a)$$

If we denote the limiting temperature referred to in (16) by T_m , and utilize therein the value of $f(T)$, viz. aT^μ , we get

$$R^{2/3} T_m^{2/3-\mu} = \frac{a}{b}. \quad (19)$$

* pV is here supposed to remain finite and positive. It will readily be seen that $\lambda = -\frac{1}{6}$ is not permissible in (15), as this would give $pV = RT/4$, whereas we ought to have $pV = RT$. There is a third possibility, viz.: $\lambda - \frac{1}{3} = 2\lambda + \frac{1}{3}$, i. e., $\lambda = -\frac{2}{3}$. This leads to $f(T)/(pV)^{5/3} = RT/pV - 1$, i. e. to $f(T) = 0$, which does not help us.

Comparing (18 a) and (19) we find

$$\left(\frac{T_m}{T_c}\right)^{1-3\mu/2} = \frac{256}{15} \quad (20)$$

The probable mean limiting value of T_m/T_c from experiment is *circa* 3. Introducing this value in (20) we find $\mu = -1.055$. The author proposes to replace this by the value minus unity. In this case, (20) shows that the derived value of T_m/T_c is 3.11, a value which is not very far from observed experimental results*. It may be noted that on van der Waals' equation, the ratio T_m/T_c is 3.375, whilst Dieterici's equation requires some modification to enable a proper value of T_m to be deduced.

The results of this section enable us to complete our equations (2), (11), and (17) in the form

$$\left[p + \frac{ap^{1/3}}{TV^{5/3}}\right](V-b) = RT \quad (21)$$

Reduced Equation of State.

- § 6. Corresponding to the equation of state (21), we have from (18) and (18 a)

$$R^2 T_c^{5/3} = \frac{15^2 a}{4^{8/3} b}, \quad (22)$$

$$p_c^5 = R^3 a^3 / (15)^3 (4b)^8. \quad (23)$$

If π , ν , and θ be the *reduced* pressure, volume, and temperature respectively, i. e. the pressure, volume, and absolute temperature respectively each expressed in terms of its critical value, we have from (21)

$$\left[\pi + \frac{\pi^{1/3}}{\theta \nu^{5/3}} \frac{a}{p_c^{2/3} V_c^{5/3} T_c}\right] \left(\nu - \frac{b}{V_c}\right) = \theta \cdot \frac{RT_c}{p_c V_c}.$$

Remembering that $V_c = 4b$, and that $RT_c/p_c V_c = 15/4$, we find after a little reduction the reduced equation of state in the simple form

$$\left[\pi + \frac{4(\pi \nu)^{1/3}}{\theta \nu^2}\right] \left(\nu - \frac{1}{4}\right) = \frac{15\theta}{4} \quad (24)$$

This may be compared with the reduced equation of van der Waals, viz.

$$\left(\pi + \frac{3}{\nu^2}\right) \left(\nu - \frac{1}{3}\right) = \frac{8\theta}{3} \quad (25)$$

The presence of the θ term in the manner indicated on the

* See, e. g., Lewis, *loc. cit.* p. 82.

left-hand side of (24) is analogous to a similar presence in the equation of Clausius*. On comparing the π correction terms of (24) and (25), it will be noticed that, in the author's proposed equation, the term $4(\pi\nu)^{1/3}/\theta$ replaces the numerical quantity 3 in (25). The other differences between (24) and (25) are numerical.

It need hardly be said that the nature of (14) implies the existence of what is sometimes called the principle of corresponding states.

State Path for Isothermal $\pi\nu$ Minima.

§ 7. We proceed to discuss more fully the conditions under which the product pV is a minimum on an isothermal, and to do this we shall use the reduced variables π , ν , and θ .

If we write (24) in the form

$$\pi\nu = \frac{15\theta\nu}{4\nu-1} - \frac{4(\pi\nu)^{1/3}}{\theta\nu},$$

we easily see that

$$\left[\frac{d(\pi\nu)}{d\nu} \right]_{\theta} = \frac{-15\theta}{(4\nu-1)^2} + \frac{4(\pi\nu)^{1/3}}{\theta\nu^2} - \frac{4(\pi\nu)^{-2/3}}{3\theta\nu} \left[\frac{d(\pi\nu)}{d\nu} \right]_{\theta},$$

from which we infer that when $\pi\nu$ is a minimum on the isothermal $\theta = \text{constant}$, i. e. when $d(\pi\nu)/d\nu = 0$,

$$15\theta^2\nu^2 = 4(\pi\nu)^{1/3}(4\nu-1)^2. \quad (26)$$

If we make $\nu \rightarrow \infty$ in this equation (and thereby take $\pi\nu = \frac{15}{4}\theta$), we find $\theta = 3.11$ in agreement with § 5.

On substituting the value of $(\pi\nu)^{1/3}$ from (26) in (24), we find

$$\theta = \frac{\pi(4\nu-1)^2}{15(4\nu-2)}. \quad (27)$$

Either (26) or (27) may be regarded as specifying the locus of the $\pi\nu$ minima. It is, however, more convenient to express this locus in terms of two variables only, and these are now taken to be π (denoted now by x) and $\pi\nu$ (denoted by y).

If we eliminate θ between (24) and (27), we find † after some reduction

$$240[4y^2 - 4xy + x^2] = y^{5/3}[16y^2 - 8xy + x^2]. \quad (28)$$

* θ similarly occurs in the equation of D. Berthelot.

† Ignoring the factor $(4y-x)$ which cancels out.

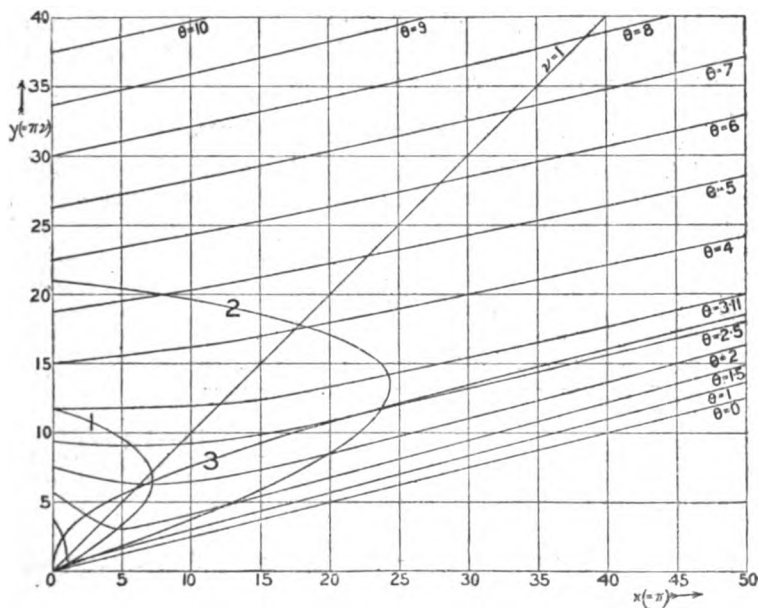
This equation can be solved as a quadratic in x , and we thus obtain

$$x = 4y[120 - y^{5/3} \pm \sqrt{60y^{5/3}}]/[240 - y^{5/3}]. \quad (29)$$

It may be verified that for x and y both positive, and $\theta > 0$ (under which circumstances $y > x/4$), the ambiguous sign is to be taken as negative, and (29) reduces to

$$x = 4y[2\sqrt{15} - y^{5/6}]/[4\sqrt{15} - y^{5/6}]. \quad (30)$$

If the positive sign be taken for the ambiguous case of (29) we should get the negative signs of (30) replaced by positive signs. The curve so obtained and running continuously from the origin would have $x = 4y$ as asymptote. The diagram (in which y is plotted against x for different isotherms) shows that under the given conditions this curve does not correspond to the physically real locus of minimum values of y on the isotherms.



The Curve (1) is $x = 4y[2\sqrt{15} - y^{5/6}]/[4\sqrt{15} - y^{5/6}]$.

" " (2) is $x = y[32\sqrt{5}y^{1/6} - 4\sqrt{2}y]/[11\sqrt{5}y^{1/6} - \sqrt{2}y]$.

" " (3) is $60x = y^{5/3}(4y - x)$.

This physically real locus given by (30) is shown in the diagram (Curve 1). It will be noticed that, starting from

the origin, the locus lies above the line $x=4y$, and ultimately x vanishes again when $y^{5/6}=2\sqrt{15}$, i. e. when $y=11.66$. This corresponds* to $\theta=3.11$. For values of y greater than that given by $y^{5/6}=4\sqrt{15}$, i. e. for $y>26.8$, there is another branch of the curve given by (30). This branch approaches asymptotically $x=4y$, but lies below this line†. It therefore does not correspond to anything physically real.

Referring to the applicable region of (30), we have

$$\frac{dx}{dy}=4-\frac{8\sqrt{15}}{[4\sqrt{15}-y^{5/6}]^2}\cdot\left[4\sqrt{15}-\frac{1}{6}y^{5/6}\right].$$

Hence $dx/dy=0$ when $y^{5/3}-\frac{23}{3}\sqrt{15}\cdot y^{5/6}+120=0$. Solving this as a quadratic in $y^{5/6}$, we find $6y^{5/6}=38.5\sqrt{15}$ or $7.5\sqrt{15}$ ‡. The former of these values corresponds to the branch of (30) lying below the line $x=4y$. The latter value (which gives $y=6.63$) corresponds to a real state of the fluid, and gives $x=7.23$, $\theta=2.06$. The state point thus obtained is that corresponding to the greatest value of x ($=\pi$) on the locus of isothermal $\pi\nu$ minima.

Joule-Thomson Inversion Curve.

§ 8. In connexion with the well-known porous-plug experiment, we have as the condition for the vanishing of the Joule-Thomson effect,

$$\theta\left(\frac{\partial\nu}{\partial\theta}\right)_{\pi}-\nu=0. \quad . \quad . \quad . \quad . \quad . \quad (31)$$

From (24) we find

$$\frac{\partial\nu}{\partial\theta}=\left[\frac{15}{4}+\frac{(4\nu-1)(\pi\nu)^{1/3}}{\theta^2\nu^2}\right]\bigg/\left[\pi+\frac{4(\pi\nu)^{1/3}}{\theta\nu^2}-\frac{5(4\nu-1)(\pi\nu)^{1/3}}{3\theta\nu^3}\right];$$

hence from (31) the inversion curve satisfies

$$\pi\nu+\frac{8(\pi\nu)^{1/3}}{3\theta\nu^2}-\frac{20(\pi\nu)^{1/3}}{3\theta\nu}=\frac{15}{4}\theta. \quad . \quad . \quad (32)$$

But from (24)

$$\pi\nu+\frac{4(\pi\nu)^{1/3}}{\theta\nu}-\frac{\pi}{4}-\frac{(\pi\nu)^{1/3}}{\theta\nu^2}=\frac{15}{4}\theta. \quad . \quad . \quad (33)$$

* When $x=0$, $\theta=4y/15$. This point is sometimes called the Boyle point.

† For then $x>4y$.

‡ Approximately.

On equating the left-hand sides of (32) and (33) we find

$$\theta = \frac{4(\pi\nu)^{1/3}}{3\pi} \left[\frac{32}{\nu} - \frac{11}{\nu^2} \right] \dots \dots \dots (34)$$

Substituting this value of θ in (24) we find

$$\left[\pi + \frac{3\pi}{32\nu - 11} \right] \left(\nu - \frac{1}{4} \right) = \frac{5(\pi\nu)^{1/3}}{\pi} \left[\frac{32}{\nu} - \frac{11}{\nu^2} \right],$$

or in terms of the variables x and y ,

$$\sqrt{2}y(4y-x) = \pm \sqrt{5}y^{1/6}(32y-11x), \quad (35)$$

which may also be written

$$x = \frac{y[32\sqrt{5}y^{1/6} \pm 4\sqrt{2}y]}{11\sqrt{5}y^{1/6} \pm \sqrt{2}y} \dots (36)$$

If the ambiguous signs in this result be taken as positive, then the ambiguous sign in (35) is to be taken negative. In this case, since physically $4y > x$, it follows that $32y < 11x$, and hence from (34) θ is negative. Thus negative signs are to be taken in (36).

The inversion curve (36) (with negative signs) is shown in the diagram (Curve 2). It will be seen that the curve closely resembles a parabola, and cuts the axis of y both at the origin and at $y^{5/6} = 8\sqrt{2}\cdot 5$, i. e. at $y = 21\cdot 0$, which corresponds to $\theta = 5\cdot 6$. In the immediate neighbourhood of the origin, x/y tends to the value $32/11$ as y diminishes, and under these circumstances an application of (24) shows that θ^2 tends to the value $512y^{1/3}/605$, and hence θ tends to zero. In this connexion it may be noted that this temperature-limit (of absolute zero) is different from the lower of the limits arising in the cases of inversion with van der Waals' or Dieterici's equations of state.

The maximum value of π on the physically real portion of (36) may be obtained by putting $dx/dy = 0$. We find

$$\frac{dx}{dy} = 4 - \frac{12\sqrt{5}[11\sqrt{5} - \frac{1}{6}\sqrt{2}y^{5/6}]}{[11\sqrt{5} - \sqrt{2}y^{5/6}]^2},$$

and equating this to zero we obtain

$$4y^{5/3} - 43\sqrt{10}y^{5/6} + 880 = 0,$$

or

$$(4y^{5/6} - 11\sqrt{10})(y^{5/6} - 8\sqrt{10}) = 0. \quad (37)$$

The diagram shows that the proper value to be taken is given by $y^{5/6} = 11\sqrt{10}/4$, i. e. $y = 13\cdot 41$, which corresponds to $x = 24\cdot 38$ and $\theta = 2\cdot 84$. In perusing the inversion curve on

the diagram given, it is to be remembered that the ordinates y only measure θ for the case of $x (= \pi) = 0$.

Variation of Specific Heat at Constant Volume with Volume.

§ 9. We proceed to investigate the variation of K_V (the specific heat at constant volume) with volume, using the well-known result

$$\left(\frac{\partial K_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V \dots \dots \dots (38)$$

We shall employ the critical values of pressure, volume, and absolute temperature as units, and write (38) in the form

$$\left(\frac{\partial K_v}{\partial v}\right)_\theta = \theta \left(\frac{\partial^2 \pi}{\partial \theta^2}\right)_v \dots \dots \dots (38a)$$

where K_v denotes the specific heat at constant volume measured as the amount of heat required to raise unit mass through a temperature range equal to the critical temperature, the heat being measured in work units with the unit of work equal to the product of the critical pressure and the critical volume.

We readily find that

$$\frac{\partial \pi}{\partial \theta} \left[1 + \frac{4(\pi v)^{1.3}}{3\theta \pi v^2}\right] = \frac{15}{4v-1} + \frac{4(\pi v)^{1.3}}{\theta^2 v^2}, \dots \dots (39)$$

from (24), and after further differentiation and reduction

$$\frac{\partial^2 \pi}{\partial \theta^2} = 120(\pi v)^{1.3}(\alpha^2 - \alpha - 1)/\theta^3 v^2(2 + \alpha)^3, \dots \dots (40)$$

where $\alpha = 15\theta/\pi(4v-1)$. Thus $\frac{\partial^2 \pi}{\partial \theta^2}$ and $\left(\frac{\partial K_v}{\partial v}\right)_\theta$ vanish when

$$\alpha^2 - \alpha - 1 = 0,$$

or for real physical conditions when $\alpha = (\sqrt{5} + 1)/2$. In this case

$$\frac{15\theta}{\pi(4v-1)} = \frac{\sqrt{5}+1}{2}, \dots \dots \dots (41)$$

which from (24) can be written as

$$\frac{4(\pi v)^{1.3}}{\theta v^2} = \frac{\pi}{2}(\sqrt{5}-1) \dots \dots \dots (42)$$

Eliminating θ from (41) and (42) we obtain

$$60(\pi v)^{1.3}/\pi^2 v^2(4v-1) = 1,$$

or

$$60x = y^{5.3}(4y-x) \dots \dots \dots (43)$$

This curve is shown in the diagram (Curve 3). It cuts the line $\nu=1$ near the isothermal $\theta=2$. We deduce that K_ν is stationary near the critical volume when θ is in the neighbourhood of 2. In this connexion, it may be observed that variations of K_ν with volume giving rise to a maximum value near the critical volume have actually been noted *, as also have analogous variations of $\left(\frac{\partial^2 p}{\partial T^2}\right)_\nu$.

From (40) it follows that $\left(\frac{\partial K_\nu}{\partial \nu}\right)_\theta$ is positive when $\alpha^2 - \alpha - 1$ is positive, i. e. when $\alpha > (\sqrt{5} + 1)/2$. Further consideration shows that this is the case when $60x > y^{5.3}(4y - x)$, that is when x has values greater than those corresponding to (43). Thus to the right of the curve (43) as shown in the diagram, K_ν increases with ν , whilst to the left of the curve the opposite is the case. The curve (43) therefore corresponds to maximum values of K_ν .

The variation of K_p with p at constant temperature can be treated using the equation $\left(\frac{\partial K_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p$, but the algebraic details are somewhat laborious. It is sufficient to note that $\left(\frac{\partial K_p}{\partial p}\right)_T$ can theoretically become infinite. It will be found that this is the case when

$$\frac{\theta^2}{(4\nu-1)^2} - \frac{(\pi\nu)^{1.3}}{9\nu^3} = 0, \quad (44)$$

in which case both $\left(\frac{\partial \theta}{\partial \nu}\right)_\pi$ and $\left(\frac{\partial \pi}{\partial \nu}\right)_\theta$ vanish. The curve (44) is thus merely the locus of points of maximum or minimum pressure on the isothermals, and clearly passes through the point which represents the critical state. In view of the fact (see below) that points of maximum or minimum pressure on the isothermals do not correspond to stable conditions, the curve (44) has only theoretical interest.

Further Details.

§ 10. We shall give here a few further points concerning (24). We can write this in the form

$$\pi + \frac{4\pi^{1.3}}{\theta\nu^{5.3}} = \frac{15\theta}{(4\nu-1)}, \quad (45)$$

which for given values of ν and θ is a cubic in $\pi^{1.3}$. There

* See Kuenen, *loc. cit.* p. 118; also H. Kammerlingh Onnes and W. H. Keesom, *loc. cit.* p. 142.

will always be one real value of $\pi^{1/3}$ satisfying (45), and since

$$\left[\frac{-15\theta}{2(4\nu-1)} \right]^2 + \left[\frac{4}{3\theta\nu^{5/3}} \right]^3 > 0,$$

for positive values of ν and θ , there will be one real value only under these circumstances*.

We can also write (24) in the form

$$f(\nu^{1/3}) \equiv \nu^{8/3} - \frac{1}{4} \left(\frac{15\theta}{\pi} + 1 \right) \nu^{5/3} + \frac{4}{\theta\pi^{2/3}} \nu^{3/3} - \frac{1}{\theta\pi^{2/3}} = 0, \quad (46)$$

which for given values of π and θ is an equation of the eighth degree in $\nu^{1/3}$. Since the pairs of successive terms involving $\nu^{7/3}$, $\nu^{6/3}$ and $\nu^{2/3}$, $\nu^{1/3}$ are absent from (46), it follows† that in general at least four of the roots are imaginary. For positive values of π and θ we have the following scheme:—

$\nu =$	$-4^{3/5}/\theta^{3/5}\pi^{2/5}$	$1/4$	$\left(\frac{15\theta}{\pi} + 1 \right) / 4$
$f =$	+	-	+

Thus there are always two real values of ν satisfying (46) under these circumstances, one lying between $\frac{1}{4}$ and

$\left(\frac{15}{\pi} + 1 \right) / 4$, the other lying between $-4^{3/5}/\theta^{3/5}\pi^{2/5}$ and $\frac{1}{4}$.

Of these, of course, only the former corresponds to a real physical state. We have thus accounted for six of the roots of (46). A plotting of a few isothermals on a π, ν diagram shows that the remaining two roots are either both real or both imaginary. For positive values of π , ν , and θ , the isothermals so drawn resemble in many ways the curves obtained with van der Waals' equation, *i.e.* for $\theta < 1$, a constant pressure-line under certain circumstances will cut an isothermal in three physically real points. For values of $\theta > 1$, a constant pressure line will cut an isothermal in only one point for which $\nu > 1/4$.

For values of $\theta < 1$, the effect of evaporation at constant pressure and temperature is represented on the π, ν diagram in the usual way by drawing a line at constant pressure π to cut the appropriate isothermal in such a way that the two

* From the general theory of Cardan's solution of the cubic.

† De Gua's Rule. See, *e.g.*, Burnside and Panton, 'Theory of Equations' (1886 ed.), p. 180.

areas bounded by the line and the isothermal are numerically equal. The saturation-curve can then be constructed from a series of such evaporation-lines. A simple analytical expression for the saturation-curve does not appear feasible*.

It is convenient to represent the various results arising from (24) by means of a diagram in which $\pi\nu$ is plotted against ν , and this has been done in the diagram appended. The arithmetical work involved can be done conveniently by taking (for a given isothermal) different values of $y (= \pi\nu)$ and solving the various quadratic equations which arise for $x (= \pi)$. The results so obtained can be utilized for determining ν if required for a π, ν diagram.

Lastly, we may note that (24) can be expressed as

$$\nu - \frac{1}{4} = \frac{15\theta}{4\pi[1 + 4(\pi\nu)^{1.3}/\theta\pi\nu^2]} = \frac{15\theta}{4\pi} - \frac{15(\pi\nu)^{1.3}}{\pi^2\nu^2} + \text{etc.}, \quad (47)$$

provided $\theta\nu(\pi\nu)^{2.3} > 4$. Under these circumstances, for large values of ν we shall have approximately

$$\nu - \frac{1}{4} = \frac{15\theta}{4\pi} - \frac{4^{5.3}}{15^{2.3}\theta^{5.3}}, \quad (48)$$

which may, *e.g.*, be compared with Callendar's equation for steam †.

Conclusion.

§ 11. The author has been led in the present paper to put forward (21) and its equivalent form (24) as a new equation of state. The chief properties of a fluid which follow this equation are as follows:

(1) For large specific volumes V , the fluid tends to follow the perfect gas law.

(2) For high pressures and low temperatures, V tends to a fixed volume b , which is taken to represent the volume of the fluid in the liquid state.

(3) The isothermals closely resemble those obtained following van der Waals' equation. Critical phenomena are indicated, and at the critical point $V = 4b$, whilst $RT/p_c V = 15/4$.

(4) Below a certain temperature ($3.11T_c$), along each isothermal the product pV first falls and then rises with

* This is true, of course, even for the simpler van der Waals' equation.

† Corresponding to the last term of (48), Callendar has a term involving $1/\theta^{10.3}$. For the region to which Callendar's equation is applicable, the steam is too much of a vapour to allow of a strict comparison with (48).

continued increase of pressure. The greatest pressure for which a minimum value of pV on an isothermal occurs is $7.23p_c$, the corresponding temperature being $2.06T_c$.

(5) Inversion in the porous-plug experiment is indicated, but this can only take place if the temperature is below $5.6T_c$. The greatest pressure which will allow of inversion is $24.36p_c$, the corresponding temperature being $2.825T_c$.

(6) The specific heat K_v at constant volume is found to vary with the volume (with the temperature constant). As the volume increases from a small value, K_v at first rises, attains a maximum value, and then diminishes. For temperatures in the neighbourhood of $2T_c$, the specific volume giving the maximum value of K_v is about the critical volume.

The chief difficulty in giving the proposed equation of state more than an empirical status lies in the fact that the pressure-correction term ϕ of (2) involves p as well as V and T .

XXXV. *A Tentative Theory of Light Quanta.*

By LOUIS DE BROGLIE*.

I. *The Light Quantum.*

THE experimental evidence accumulated in recent years seems to be quite conclusive in favour of the actual reality of light quanta. The photoelectric effect, which is the chief mechanism of energy exchange between radiation and matter, seems with increasing probability to be always governed by Einstein's photoelectric law. Experiments on the photographic actions, the recent results of A. H. Compton on the change in wave-length of scattered X-rays, would be very difficult to explain without using the notion of the light quantum. On the theoretical side Bohr's theory, which is supported by so many experimental proofs, is grounded on the postulate that atoms can only emit or absorb radiant energy of frequency ν by finite amounts equal to $h\nu$, and Einstein's theory of energy fluctuations in the black radiation leads us necessarily to the same ideas.

I shall in the present paper assume the real existence of light quanta, and try to see how it would be possible to reconcile with it the strong experimental evidence on which was based the wave theory.

For the sake of simplicity, it is a very natural assumption to admit that all light quanta are identical and that only

* Communicated by R. H. Fowler, M.A.

their velocities are different. We shall then assume that the "mass at rest" of every light quantum has a given value m_0 : since the atoms of light have velocities very nearly equal to the Einstein's limiting velocity c , they must have an extremely small mass (not infinitely small in a mathematical sense); the frequency of the corresponding radiation must be related to the whole energy of a quantum by the relation

$$h\nu = \frac{m_0 c^2}{\sqrt{1-\beta^2}}, \quad \left(\beta = \frac{v}{c}\right);$$

but, since $1-\beta^2$ is very small, we can write

$$\beta = \frac{v}{c} = 1 - \frac{1}{2} \frac{m_0^2 c^4}{h^2 \nu^2}.$$

The light quanta would have velocities of slightly different values, but such that they cannot be discriminated from c by any experimental means. It then seems that m_0 should be at most of the order of 10^{-50} gr.

Naturally, the light quantum must have an internal binary symmetry corresponding to the symmetry of an electromagnetic wave and defined by some axis of polarization. We shall refer again later to this remark.

II. *The Black Radiation as a Gas of Light Quanta.*

Let us consider a gas made up by the light quanta we have described above. At a given temperature (not too near to the absolute zero) almost all these atoms of light would have velocities $v=\beta c$ very nearly equal to c . The whole energy of one of these atoms is

$$W = \frac{m_0 c^2}{\sqrt{1-\beta^2}},$$

and its momentum is

$$G = \frac{m_0 v}{\sqrt{1-\beta^2}};$$

so we have approximately

$$G = \frac{W}{c}.$$

The pressure of such a gas on the walls of the enclosure is easily seen to be

$$p = \frac{n}{6} \cdot 2Gc = \frac{1}{3}nW,$$

if n is the number of light quanta in an element of volume.

This expression is the same as the one given by the electromagnetic theory, whilst without using the Relativity formulæ we should have found a result twice as great as this.

Now the question arises, Can we use for the quanta gas Maxwell's energy partition law? In Einstein's dynamics, Liouville's theorem, on which is based all Statistical Dynamics, is still valid; we can then use for the elementary cell of extension-in-phase a value proportional to $dx dy dz dp dq dr$, if x, y, z are rectangular coordinates and p, q, r the corresponding momenta. In consequence of the canonical distribution law, the number of atoms whose representative points are in the element $dx dy dz dp dq dr$ must be proportional to

$$e^{-\frac{W}{kT}} dx dy dz dp dq dr = e^{-\frac{W}{T}} \cdot 4\pi G^2 dG dv,$$

if dv is the element of volume and G the momentum. But, since $G = \frac{W}{c}$, this number is also given by

$$C' \times e^{-\frac{W}{kT}} u^2 dv dv.$$

Each quantum has a total energy $h\nu$; then the whole energy contained in the volume dv and carried by light quanta of energy $h\nu$ is

$$C' e^{-\frac{h\nu}{kT}} \nu^3 dv dv.$$

This is obviously Wien's limiting form of the radiation law. Two years ago * I was able to show that, by using the hypotheses made by Planck that the element of extension in phase was $\frac{1}{h^3} dx dy dz dp dq dr$, it was possible to find for the radiant energy density the value

$$u_\nu dv = \frac{8\pi h}{c^3} \nu^3 e^{-\frac{h\nu}{kT}} dv.$$

This was an encouraging result, but not quite complete. The assumption of finite elements of extension in phase seemed to have a somewhat arbitrary and mysterious character. Moreover, Wien's law is only a limiting form of the actual radiation law, and I was obliged to suppose some kind of quanta aggregation for explaining the other terms of the series.

It seems that these difficulties are now removed, but we shall first of all explain many other ideas; we shall later on return to the "black radiation" gas.

* See *Journal de Physique*, November 1922.

III. An important Theorem on the Motion of Bodies.

Let us consider a moving body whose "mass at rest" is m_0 ; it moves with regard to a given observer with velocity $v = \beta c$ ($\beta < 1$). In consequence of the principle of energy inertia, it must contain an internal energy equal to $m_0 c^2$. Moreover, the quantum relation suggests the ascription of this internal energy to a periodical phenomenon whose frequency is $\nu_0 = \frac{1}{h} m_0 c^2$. For the fixed observer, the whole energy is $\frac{m_0 c^2}{\sqrt{1-\beta^2}}$ and the corresponding frequency is $\nu = \frac{1}{h} \frac{m_0 c^2}{\sqrt{1-\beta^2}}$.

But if the fixed observer is looking at the internal periodical phenomenon, he will see its frequency lowered and equal to $\nu_1 = \nu_0 \sqrt{1-\beta^2}$, that is to say this phenomenon seems for him to vary as $\sin 2\pi \nu_1 t$. The frequency ν_1 is widely different from the frequency ν ; but they are related by an important theorem which gives us the physical interpretation of ν .

Let us suppose that, at time 0, the moving body coincides in space with a wave whose frequency ν has the value given above and which spreads with velocity $\frac{c}{\beta} = \frac{c^2}{v}$. This wave,

however, cannot carry energy, according to Einstein's ideas,

Our theorem is the following:—"If, at the beginning, the internal phenomenon of the moving body is in phase with the wave, this harmony of phase will always persist." In fact, at time t , the moving body is at a distance from the origin $x = vt$ and its internal phenomenon is proportional

to $\sin 2\pi \nu_1 \frac{x}{v}$; at the same place the wave is given by

$\sin 2\pi \nu \left(t - \frac{\beta x}{c} \right) = \sin 2\pi \nu x \left(\frac{1}{v} - \frac{\beta}{c} \right)$. The two sines will be equal; the harmony of phase will again occur if the following condition is realized :

$$\nu_1 = \nu(1-\beta^2),$$

a condition clearly satisfied by the definitions of ν and ν_1 .

This important result is implicitly contained in Lorentz's time transformation. If τ is the local time of an observer carried along with the moving body, he will define the

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internal phenomenon by the function $\sin 2\pi\nu_0\tau$. According to Lorentz's transformation, the fixed observer must describe the same phenomenon by the function $\sin 2\pi\nu_0 \frac{1}{\sqrt{1-\beta^2}} \left(t - \frac{\beta x}{c}\right)$, which can be interpreted as the representation of a wave of frequency $\frac{\nu_0}{\sqrt{1-\beta^2}}$ spreading along the x axis with velocity $\frac{c}{\beta}$.

We are then inclined to admit that any moving body may be accompanied by a wave and that it is impossible to disjoin motion of body and propagation of wave.

This idea can also be expressed in another way. A group of waves whose frequencies are very nearly equal has a "group velocity" U , which has been studied by the late Lord Rayleigh, and which in the usual theory is the velocity of "energy propagation." This group velocity is linked with the "phase velocity" V by the relation

$$\frac{1}{U} = \frac{d\left(\frac{\nu}{V}\right)}{d\nu}.$$

If ν is equal to $\frac{1}{h} \frac{m_0 c^2}{\sqrt{1-\beta^2}}$ and V to $\frac{c}{\beta}$, we find $U = \beta c$ —that is to say, "*The velocity of the moving body is the energy velocity of a group of waves having frequencies $\nu = \frac{1}{h} \cdot \frac{m_0 c^2}{\sqrt{1-\beta^2}}$ and velocities $\frac{c}{\beta}$ corresponding to very slightly different values of β .*"

IV. Dynamics and Geometrical Optics.

Trying to extend the former ideas to the case of variable velocity is a rather difficult but very suggestive problem. If in any medium a moving body describes a curved path, we say that there is a field of force; at each point the potential energy may be calculated, and the body when crossing this point has a velocity determined by the constant value of its whole energy. Now, it seems natural to suppose that the phase wave must have at any point a velocity and a frequency fixed by the value which β would have if the body were there. During its propagation the phase wave has a constant frequency ν and a constantly variable velocity V .

Perhaps a new electromagnetism will give us the laws of this complicated propagation, but it seems that we know beforehand the final result: "*The rays of the phase wave are identical with the paths which are dynamically possible.*" In fact, the paths of the rays can be computed as in a medium of variable dispersion by means of Fermat's principle, which may be written here (λ wave-length, ds element of path):

$$\delta \int \frac{ds}{\lambda} = \delta \int \frac{v ds}{V} = \delta \int -\frac{m_0 \beta c}{\sqrt{1-\beta^2}} ds = 0.$$

The principle of least action in its Maupertuisian form gives the dynamical paths by the equation

$$\begin{aligned} \delta \int m_0 c^2 \left(\frac{1}{\sqrt{1-\beta^2}} - \sqrt{1-\beta^2} \right) dt \\ = \delta \int \frac{m_0 \beta^2 c^2}{\sqrt{1-\beta^2}} dt = \delta \int \frac{m_0 \beta c}{\sqrt{1-\beta^2}} ds = 0, \end{aligned}$$

a result which justifies the above statement.

It is now so simple a matter to show that the theorem of phase harmony is always valid that it seems not necessary to develop the proof.

The present theory suggests an interesting explanation of Bohr's stability conditions. At time 0 the electron is in a point A of its trajectory. The phase wave starting at this instant from A will describe all the path and meet again the electron in A'. It seems quite necessary that the phase wave shall find the electron in phase with itself. This is to say: "The motion can only be stable if the phase wave is tuned with the length of the path." The tune relation is then:

$$\int \frac{ds}{\lambda} = \int_0^T \frac{m_0 \beta^2 c^2}{h \sqrt{1-\beta^2}} dt = n$$

(n whole number; T revolution period).

Now, we can write the stability condition of the quantum theory in a general form given by Einstein which degenerates into the manifold Sommerfeld's conditions for quasi-periodical cases in consequence of the infinite number of the pseudo-periods. Let us call $p_x p_y p_z$ the momenta; then Einstein's general condition is

$$\int (p_x dx + p_y dy + p_z dz) = n\hbar \quad (n \text{ whole number}),$$

or also

$$\int_0^T \frac{m_0}{\sqrt{1-\beta^2}} (v_x^2 + v_y^2 + v_z^2) dt = \int_0^T \frac{m_0}{\sqrt{1-\beta^2}} \beta^2 c^2 dt = nh,$$

which is precisely the result obtained above.

V. *The Propagation of Light Quanta and the Coherence Problem.*

We will now make use of our results for studying the propagation of free light quanta whose velocities are always slightly lower than c . We can say: "The atom of light whose whole energy is equal to $h\nu$ is the seat of an internal periodical phenomenon which, for a fixed observer, has at each point of space the same phase as a wave spreading in the same direction with velocity very nearly equal to c (very little greater)." The light quantum is in some manner a part of the wave, but for explaining interferences and other phenomena of the wave optics it is necessary to see how several light quanta can be parts of the same wave. This is the coherence problem.

In the light quanta theory, it seems necessary to make the following hypothesis: "When a phase wave crosses an excited atom, this atom has a certain probability of emitting a light quantum determined at each instant by the intensity of the wave." Perhaps this hypothesis will seem arbitrary, but I think that any theory of coherence must adopt some postulate of this kind.

The emissions of γ -rays by radioactive substances are known to be quite independent, but this cannot be considered as an objection against our view because the "mean life" of any known radioactive atom is always so much greater than the period of the γ -rays.

Thus when an atom emits a light quantum, a spherical phase wave is simultaneously emitted and, crossing over the neighbouring atoms of the point source, will excite other emissions. The non-material phase wave will carry many little drops of energy which slide slowly upon it and whose internal phenomena are coherent.

VI. *Diffraction by a Screen Edge and the Inertia Principle.*

The corpuscular theory of light meets here a great difficulty. It is known since Newton that the light rays passing within a short distance of a screen edge are no longer straight

but that some penetrate into the geometrical shadow. Newton ascribed this deviation to the action of some forces which would be exerted by the edge upon the light corpuscle. It seems to me that this phenomenon is perhaps worthy of a more general explanation. Since an intimate connexion seems to exist between motion of bodies and propagation of waves, and since the rays of the phase wave may now be considered as the paths (the possible paths) of the energy quanta, we are inclined to give up the inertia principle and to say: "A moving body must always follow the same ray of its phase wave." In the continuous spreading of the wave, the form of the surfaces of equal phase will change continuously and the body will always follow the common perpendicular to two infinitely near surfaces.

When Fermat's principle is no longer valid for computing the ray path, the principle of least action is no longer valid for computing the body path. I think that these ideas may be considered as a kind of synthesis of optics and dynamics.

We must still specify some points. The ray which now assumes in our ideas an important physical significance may be defined as above by the *continuous* spreading of a small part of the phase wave: it cannot be defined at each point by the geometrical sum for all the waves of the vector which is called in electromagnetic theory "radiant or Poynting's vector." Let us consider a sort of Wiener's experiment. We send a train of plane waves on a perfectly reflecting plane mirror in the normal direction; standing waves are set up; the reflecting mirror is a nodal plane for the electric vector, the plane at a distance $\frac{1}{4}\lambda$ from the mirror is a nodal plane for the magnetic vector, the plane at a distance $\frac{1}{2}\lambda$ of the mirror is again a nodal plane for the electric vector, and so on. In each nodal plane the radiant vector is null. May we say that these planes are not crossed by any energy? Evidently not, we can only say that the interference states in these planes are always the same. In every interference case we should find similar intricacies. In the wave theory, the propagation of energy has a somewhat fictitious character, but, in return, the exact calculation of the interference fringes is easily made; we shall try in the next paragraph to see why it is so.

VII. *A new Explanation of Interference Fringes.*

Consider how we can detect the presence of light at a point in space—by direct perception of the scattered light, by photographic tests, by calorific effects, and perhaps by some

other means. It seems that all these means can, in fact, be reduced to photoelectric actions and scattering. Now, when a light quantum crosses a material atom, it has a certain probability of being absorbed or scattered, which can depend on external agencies. If then a theory succeeds in determining these probabilities without taking account of the actual motion of energy, it may be able to predict correctly the average reaction between radiation and matter at each place. Following the electromagnetic theory (and Bohr's correspondence principle is consistent with this view) I have been inclined to suppose that, for a material atom, the probability of absorbing or scattering a light quantum is determined by the geometrical sum of one of the defining vectors of the phase waves crossing upon it. The last hypothesis is, in fact, quite analogous to that which is admitted by electromagnetic theory when it links intensity of disclosable light with the intensity of the resultant electric vector. Thus, in the Wiener's experiment, the photographic action only occurs in the nodal planes of the electric vector; according to the electromagnetic theory, the luminous magnetic energy is not disclosable.

Let us now consider Young's interference experiment. Some atoms of light pass through the holes and diffract along the ray of the neighbouring part of their phase waves. In the space behind the wall, their capacity of photoelectric action will vary from point to point according to the interference state of the two phase waves which have crossed the two holes. We shall then see interference fringes, however small may be the number of diffracted quanta, however feeble may be the incident light intensity. The light quanta do cross all the dark and bright fringes; only their ability to act on matter is constantly changing. This kind of explanation, which seems to remove at the same time the objections against light quanta and against the energy propagation through dark fringes, may be generalized for all interference and diffraction phenomena.

VIII. *The Quanta and the Dynamical Theory of Gases.*

For the sake of calculating the entropy constants and the so-called "chemical constants," Planck and Nernst have been obliged to introduce the quantum idea into the theory of gases. As explained above, Planck chooses an element of extension in phase equal to

$$\frac{1}{h^3} dx dy dz dp dq dr \quad \text{or} \quad \frac{4\pi}{h^3} m_0^{3/2} \sqrt{2\pi c} dw dx dy dz.$$

We shall now try to justify this assumption.

Each atom of velocity βc may be considered as linked with a group of waves whose phase velocity is $V = \frac{c}{\beta}$, frequency $\frac{1}{h} \frac{m_0 c^2}{\sqrt{1-\beta^2}}$, and group velocity $U = \beta c$. The state of the gas can only be stable if the waves corresponding to all the atoms make up a system of standing waves. Using a well-known method given by Jeans, we find for the number of waves per unit of volume whose frequencies are included in the interval $\nu, \nu + d\nu$ * :

$$n_\nu d\nu = \frac{4\pi}{U V^2} \nu^2 d\nu = \frac{4\pi}{c^3} \beta \nu^2 d\nu.$$

If w is the kinetic energy of an atom and ν the corresponding frequency, then :

$$h\nu = \frac{m_0 c^2}{\sqrt{1-\beta^2}} = w + m_0 c^2 = m_0 c^2 (1 + \alpha),$$

where $\alpha = \frac{w}{m_0 c^2}$.

It is now very easy to find that $n_\nu d\nu$ is given by the equation :

$$n_\nu d\nu = \frac{4\pi}{h^3} m_0^2 c (1 + \alpha) \sqrt{\alpha(2 + \alpha)} dw.$$

Each phase wave can carry with it one, two, or more atoms, so that, according to the canonical law, the number of atoms whose energy is $h \cdot \nu$, will be proportional to :

$$\frac{4\pi}{h^3} m_0^2 c (1 + \alpha) \sqrt{\alpha(2 + \alpha)} dw dx dy dz \sum_1^\infty e^{-\frac{nh\nu}{kT}}.$$

Let us first consider a material gas whose atoms have relatively great mass and relatively small velocities. We can then neglect all the terms of the series except the first, and we can also put $1 + \alpha = 1$. The number of atoms whose kinetic energy is w will be, neglecting a constant factor,

$$\frac{4\pi}{h^3} m_0^{3/2} \sqrt{2w} dw dx dy dz e^{-\frac{w}{kT}},$$

a result which justifies Planck's method and leads to the usual form of Maxwell's law.

In the case of the light quanta gas α is always great, and, moreover, we must use all the series. In consequence of the

* Léon Brillouin, *Théorie des Quanta*, p. 38. Paris : A. Blanchard.

internal binary symmetry of the light quantum, we must introduce a factor 2, and we find that the radiant energy density is proportional to :

$$\frac{8\pi}{h^3 c^3} w^3 \sum_1^{\infty} e^{-\frac{n h \nu}{kT}} d w = \frac{8\pi h}{c^2} \frac{\nu^3}{e^{\frac{h \nu}{kT}} - 1} d \nu.$$

A method developed in the *Journal de Physique*, of November 1922, shows that the proportionality factor is unity, so that we obtain the actual radiation law.

IX. Open Questions.

The conceptions stated in this paper, if they are received, will necessitate a wide modification of the electromagnetic theory. The so-called "electric and magnetic energies" must be only a kind of average value, all the real energy of the fields being probably of a corpuscular fine-grained structure. The building up of a new electromagnetism seems to be a very difficult task, but we have one directive idea : according to the correspondence principle and to the above statements, the defining vectors of the old electromagnetic theory would give the probability of the reaction between matter and the fine-grained energy.

The new electromagnetism will give the solution of many problems. The laws of propagation of waves given by Maxwell's theory will probably be valid for the energyless light phase waves, and the scattering of the radiant energy will be explained by the resulting curvature of the rays (viz., light quanta paths). There seems to be a great analogy between scattering of radiation and scattering of corpuscles ; lowering of particles' velocities by crossing through a screen may also be similar to the lowering of X-ray frequencies by scattering, which recently has been computed and experimentally checked by A. H. Compton.

Explaining optical dispersion will be more difficult. The classical theories (including the electron theory) gives only an average view of this phenomenon, which is produced by complex elementary reactions between radiation and atoms ; we shall certainly be obliged here also to distinguish accurately the real motion of energy from the propagation of the resulting interference state. The kind of "resonance" shown by the variations of refractive index seems no longer to be irreconcilable with discontinuity of light.

Many other questions remain open : What is the mechanism

of Bragg's absorption? What occurs when an atom passes from a stable state to another, and how does it eject a single quantum? How may we introduce the granular structure of energy into our conceptions of elastic waves and into Debye's theory of specific heats?

Finally, we must remark that the quantum relation remains still a kind of postulate defining the constant h whose actual significance is not at all cleared up; but it seems that the quantum enigma is now reduced to this unique point.

Summary.

In the present paper it is assumed that the light is essentially made up of light quanta, all having the same extraordinarily small mass. It is shown mathematically that the Lorentz-Einstein transformation joined with the quantum relation leads us necessarily to associate motion of body and propagation of wave, and that this idea gives a physical interpretation of Bohr's analytical stability conditions. Diffraction seems to be consistent with an extension of the Newtonian Dynamics. It is then possible to save both the corpuscular and the undulatory characters of light, and, by means of hypotheses suggested by the electromagnetic theory and the correspondence principle, to give a plausible explanation of coherence and interference fringes. Finally, it is shown why quanta must take a part in the dynamical theory of gases and how Planck's law is the limiting form of Maxwell's law for a light quanta gas.

Many of these ideas may be criticized and perhaps reformed, but it seems that now little doubt should remain of the real existence of light quanta. Moreover, if our opinions are received, as they are grounded on the relativity of time, all the enormous experimental evidence of the "quantum" will turn in favour of Einstein's conceptions.

1 October, 1923.

Note.—Since I have written this paper, I have been able to give to the results contained in the fourth section a somewhat different, but much more general form.

The principle of least action for a material point can be expressed in the space-time notation by the equation:—

$$\delta \int_1^4 J_i dx_i = 0,$$

if the J_i are the covariant components of a four-dimensional

vector whose time component is the energy of the point divided by c and space components are the components of its momentum.

Similarly, in studying the propagation of waves, we have to write :—

$$\delta \int_1^4 O_i dx^i = 0,$$

if the O_i are the covariant components of a four-dimensional vector whose time component is the frequency divided by c and space components the components of a vector drawn along the ray and equal to $\frac{\nu}{V} = \frac{1}{\lambda}$ (V phase velocity).

Now, the quantum relation says that $J_4 = h O_4$. More generally, I suggest putting $\vec{J} = h \vec{O}$. From this statement, the identity of the two principles of Fermat and Maupertius follows immediately, and it is possible to deduce rigorously the velocity of the phase wave in any electromagnetic field.

XXXVI. *The Kinetic Energy of Electrons emitted from a Hot Tungsten Filament in an Atmosphere of (a) Argon (b) Hydrogen.* By J. F. CONGDON, B.Sc., A.Inst.P., King's College, London*.

RECENT experiments by J. H. Jones †, L. H. Germer ‡, and H. H. Potter § have shown conclusively that the electrons emitted from hot metals *in vacuo* possess kinetic energy in accordance with Maxwell's distribution law.

This paper deals with experiments on the kinetic energy of the electrons emitted from a hot tungsten filament in (a) an atmosphere of argon, (b) an atmosphere of hydrogen.

The kinetic energy of the electrons emitted from hot platinum in hydrogen has been measured by Mr. H. H. Potter, who found that for pressures of the gas greater than 50×10^{-3} mm., the slopes of the curves obtained by plotting the logarithms of the thermionic currents against the corresponding applied retarding voltages were less than

* Communicated by Prof. O. W. Richardson, F.R.S.

† Proc. Roy. Soc. vol. cii. p. 734 (1923).

‡ Science, vol. lvii. p. 392 (1923).

§ Phil. Mag. vol. xlv. p. 768 (Nov. 1923).

in vacuo, but that in every case the linear relation required by Maxwell's law held.

The apparatus used in the experiments described here was similar to that used by H. H. Potter, and for a description reference should be made to his paper.

The method of measuring the kinetic energy of the electrons was that used by J. H. Jones in the latter part of his work.

Temperature of the Filament.

It was not necessary to know the temperatures of the filament in these experiments, but it was found useful to determine them in order to test the accuracy of the experiment by a comparison of the slopes of the curves obtained *in vacuo* with the theoretical values. The resistances of the filament at room temperatures and high temperatures were calculated from the condition of the balance of the Wheatstone bridge; and the temperature of the hot filament was estimated from its change in resistance by means of data given by Langmuir* for tungsten. The introduction of gas into the tube reduced the resistance of the hot filament, but did not affect that of the cold filament appreciably. Therefore to keep the hot filament at the same temperature as *in vacuo*, it was only necessary to increase the heating current until a balance of the Wheatstone bridge was restored and the resistance of the filament had the same value as *in vacuo*.

It was usually found that the initial electron emission was not uniform. This was probably due to some compound which formed on the surface of the filament during the process of cooling. Prolonged heating (about two hours) of the filament in a high vacuum at a high temperature, however, got rid of this effect, and the emission gradually assumed a constant value. It was therefore necessary to heat the filament in a high vacuum until the emission was constant before taking a set of observations, after a filament had been allowed to cool.

The argon used in these experiments was prepared commercially and supplied in cylinders by the British Oxygen Co. It contained an appreciable quantity of oxygen and nitrogen, and therefore had to be purified before being admitted into the thermionic tube. This was done by passing it over small pieces of heated calcium contained in three small porcelain boats inside a long unglazed silicon tube

* Phys. Rev. vol. vii. no. 3 (March 1916).

which was heated by surrounding it with a small electric furnace. Calcium only absorbs oxygen and nitrogen when they are present in small quantities, so it was not always possible to obtain argon entirely free from oxygen when the pressure of argon was comparatively large, *e. g.* 1 cm.; and filaments fused quickly if oxygen were present to any extent. A comparatively pure sample at a high pressure was obtained eventually, and thermionic currents in argon at a pressure of 5.5 cm. were obtained.

The purity of the argon was tested by examining its spectrum produced in a small vacuum discharge-tube. This, however, is not a very delicate test, since oxygen and nitrogen may be present in small quantities without being detected spectroscopically.

The hydrogen used was obtained by heating a palladium tube connected to the apparatus. The gas obtained in this way was very pure and free from oxygen, with the result that no fusing of filaments took place.

The method of experiment was to obtain a current-potential curve at a constant temperature of the filament in high vacuum (about 1×10^{-6} mm. pressure), and then repeat the curve with various pressures of gas in the thermionic tube at the same temperature of the filament.

The currents in high vacua were all measured with the pumps working.

Since the value of $\log i/i_0$ is independent of the units in which the current is measured, the current in all the curves is expressed in terms of the galvanometer deflexion.

The linear relation between $\log i/i_0$ and V only holds for low values of the current, and since at these retarding voltages it is only a small fraction of the saturation current, the observations were difficult to take and were liable to big percentage error unless the saturation currents had high values.

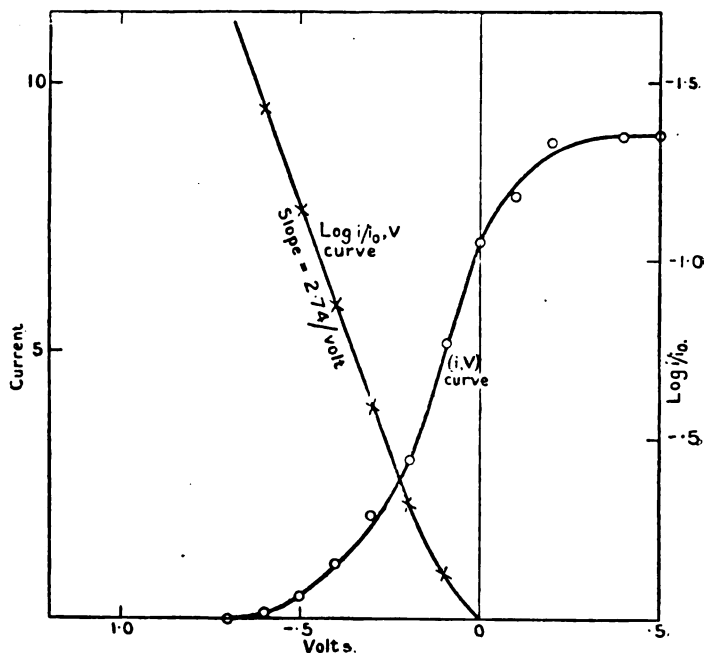
RESULTS OF OBSERVATIONS.—(a) ARGON.

Experiment 1.—Length of filament = 3.5 cm., diameter = 0.005 cm. The tube was heated in the furnace for about two hours and the filament, during cooling, glowed for about two hours until the thermionic emission was constant.

Temperature of filament = 1650° K.

Three curves similar to fig. 1 were obtained, showing the relation between the current and the applied potential.

Fig. 1.



Pressure of Argon = $\frac{1.20}{1000}$ mm. Temp. = 1650° K.

The following results were obtained:—

Pressure of Argon.	Slope of $(\log i/i_0, V)$ Curve.
0 mm.	2.76
183×10^{-3} „	2.90
120×10^{-3} „	2.74

Theoretical slope in vacuum = 2.85.

Experiment 2.—A new filament of the same dimensions as that used in Experiment 1.

Tube heated in electric furnace for one hour and the filament afterwards glowed for about two hours.

Temperature of filament = 1500° K.

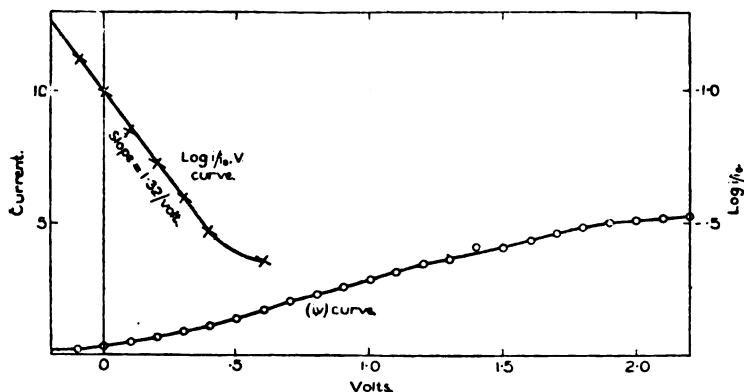
Two current-potential curves were obtained and gave the following results:—

Pressure of Argon.	Slope of $(\log i/i_0, V)$ Curve.
0 mm.	2.95
140×10^{-3} „	2.94

Theoretical slope in vacuum = 3.14.

Experiment 3.—The same filament as used in Experiment 2.
 Temperature of filament = 1800° K.

Fig. 2.



Pressure of Argon = 4.5 cm. Temp. = 1800° K.

Ten curves were obtained and gave the following results :—

Pressure of Argon.	Slope of ($\log i/i_0$, V) Curve.
0 mm.	2.51
240×10^{-3} "	2.455
150×10^{-3} "	2.71
100×10^{-3} "	2.48
70×10^{-3} "	2.55
0 "	2.50
2.0 cm.	2.60
3.0 "	2.62
4.5 "	1.32
5.5 "	1.75

Theoretical slope = 2.55.

(b) HYDROGEN.

Experiment 4.—The copper cylinder used in the previous experiments was thoroughly cleaned and the tungsten filament replaced by another having the same dimensions.

The tube and cylinder were heated for about $2\frac{1}{2}$ hours in the electric furnace, and the filament glowed for about two hours in a high vacuum.

Temperature of filament = 1900° K.

Five curves were obtained and gave the following results :—

Pressure of Hydrogen.	Slope of $(\log i/i_0, V)$ Curve.
0×10^{-3} mm.	2.39
150×10^{-3} „	1.65
80×10^{-3} „	1.44
125×10^{-3} „	1.586
185×10^{-3} „	2.085

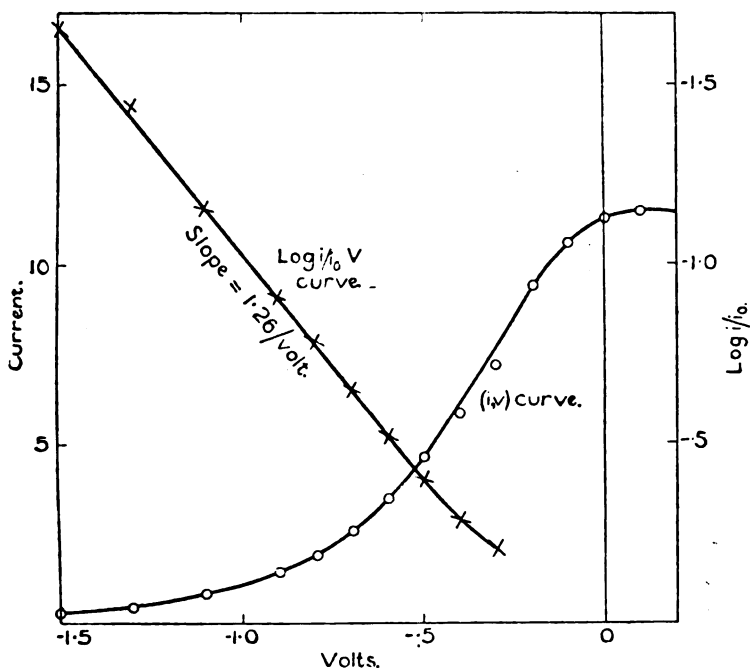
Theoretical slope = 2.45.

Experiment 5.—A new filament was used having the same dimensions as the previous one.

The copper cylinder was quite clean, so it was not necessary to heat in the electric furnace. The filament was glowed for about two hours in a high vacuum.

Temperature of filament = 1600°K .

Fig. 3.



Pressure of Hydrogen = $\frac{2.50}{1000}$ mm. Temp. = 1600°K .

Seven curves were obtained and gave the following results :—

Pressure $\times 10^{-3}$ mm.	Slope of $(\log i/i_0, V)$ Curve.
0	2.96
235	1.99
80	1.78
135	2.25
175	2.86
110	2.27
250	1.26

Theoretical slope = 2.94.

DISCUSSION OF RESULTS.

The slopes of $(\log i/i_0, V)$ curves have been obtained for electrons emitted from a hot tungsten filament in high vacuum, and give results in close agreement with those demanded by Maxwell's distribution law.

The slopes of the curves have also been obtained in pressures of argon ranging from 70×10^{-3} mm. to 50 mm. The results clearly indicate that up to a pressure of 3 cm. the linear relation is maintained and the slopes have the same values as *in vacuo*. At pressures of argon of 4.5 cm. and above the linear relation still holds, but the slopes are much less than those for the corresponding temperature obtained *in vacuo*. The reason for this sudden drop in slope is not clear. It is hardly possible that it is due to an increase in the energy of the electrons; but it may be due to local fields at the surface of the filament. Impurities in the gas may also account in some way for the change in slope.

The curves for hydrogen give quite different results. In nearly every case the slopes of the $(\log i/i_0, V)$ curves have values which are considerably lower than those for the corresponding temperature obtained *in vacuo*. The linear relation, however, has been found to hold for low values of the current.

The slope of the curves does not in any way appear to be a function of the pressure of the hydrogen, although the results of Experiment 4 seem to indicate that the slope increases with increasing pressure. This conclusion, however, is not confirmed by the results of Experiment 5, in which the slopes bear no relation at all to the pressure of the hydrogen. For example, the slope at a pressure of 110×10^{-3} mm. is 2.27, and for a pressure of 250×10^{-3} mm. it is 1.26.

The change seems to depend somewhat on the previous

treatment of the filament. With curves obtained immediately after admitting the hydrogen, the slope was usually much less than that obtained *in vacuo*; but if the cold filament were allowed to remain in the gas for any length of time before taking the curve, the slope tended towards the normal value. Further investigation of this point, however, is necessary before arriving at a definite conclusion.

The general results obtained in hydrogen agree closely with those obtained by Mr. Potter for platinum in hydrogen.

The low slopes obtained in hydrogen are not satisfactorily accounted for. They cannot in any way be due to the pressure of the gas and the consequent decrease in the length of the mean free path, as in that case the same effect on the slope would be expected in argon and some definite relation would exist between the slope and the pressure of the gas; but the slopes in argon are the same as *in vacuo* and are unaffected by the pressure of the gas.

They may arise on account of local fields at the surface of the filament, but since the current-potential curves saturate easily in hydrogen, this view is not readily supported. Prof. Richardson has made the suggestions (1) that owing to the pressure of hydrogen the surface of the filament is in a state of polarization, and that consequently the electrons are emitted with a velocity above the normal; (2) that the electrons may start with a Maxwell distribution which is subsequently modified by local fields, thus giving rise to abnormal measured values.

In any case hydrogen has some peculiar property not possessed by argon.

CONCLUSIONS.

(1) The average energy of the electrons emitted from a hot tungsten filament *in vacuo* is in close agreement with the requirements of Maxwell's distribution law.

(2) The presence of argon over a wide range of pressures has no effect on the measured average energy.

(3) The presence of hydrogen, even at low pressures, appears to increase the measured average energy considerably whilst maintaining the linear relation of the ($\log i/i_0$, $\sqrt{V}$) curve.

I wish to thank Prof. O. W. Richardson for suggesting this research and for his advice and interest during the course of the experiments.

Phil. Mag. Ser. 6. Vol. 47. No. 278. Feb. 1924. 2 H

XXXVII. *On Soft X-Rays from Carbon.* (Preliminary communication.) By P. I. LUKIRSKY, *Lecturer in Physics, Petrograd University* *.

THE filling of the gap between short ultra-violet and soft Röntgen rays presents some interest in addition to the effect of obtaining a continuous scale of electromagnetic waves. The determination of the characteristic wave-lengths of the lightest elements—and it is precisely these waves which lie in the above gap—is of great importance in the question of atomic structure, for the laws of atomic dynamics must take a particularly simple form with respect to the light elements containing a relatively small number of electrons. For instance, in the case of carbon, which has been the object of our investigation, each atom contains but six electrons, of which two form the K-group and four the L-group, coinciding with the optical one. The extreme ultra-violet spectrum of carbon has been recently investigated by Millikan, who succeeded by means of his diffraction grating in extending it to 202 Å and later to 136 Å .

On the other hand, soft X-rays have been measured by the crystal method up to wave-lengths of 12 Å . In order to measure wave-lengths within the interval $12\text{--}136\text{ Å}$, we may avail ourselves of the photo-electric action, *i. e.* of the secondary cathode rays streaming from a metal surface illuminated by X-rays. This was the principle of the method used in the experiments of Richardson, Kurth, Hughes, McLennan, and Holtsmark. These authors measured the total photo-electric current due to X-rays of a given substance, or rather a given anti-cathode bombarded by primary cathode rays of gradually increasing speed.

When the energy of these primary electrons (*i. e.* the voltage applied) is small, the anti-cathode emits a continuous Röntgen spectrum only, whose intensity gradually increases along with the voltage, causing a corresponding increase of the secondary current. When the energy of the primary electrons is large enough to excite the emission of characteristic rays, the rate of increase must abruptly change, which will be manifested by a break on the curve: secondary current-voltage. In this way the limiting energy of eV (V , voltage; e , electronic charge) of the K and L series of various light elements has been determined, and from it the

* Communicated by the Author.

limiting frequency ν deduced by means of the quantum relation

$$h\nu = eV,$$

where h is Planck's constant.

The above method does not permit the direct determination of the wave-length of the characteristic lines *emitted* by the substance considered. Besides, when the energy of the primary electrons but slightly exceeds the limiting energy of an X-ray series, the characteristic spectrum, as well known, is very weak. Therefore, the exact position of the break cannot be determined accurately, as is clearly seen from the great divergence of the results obtained by various authors for the same series under apparently identical conditions.

It is well known that the maximum velocity of secondary electrons generated by ordinary, ultra-violet, and Röntgen rays is given by Einstein's relation

$$\frac{1}{2}mv^2 = h\nu - p_1 - p_2,$$

where m is the mass, v the velocity of the electrons, ν the frequency of rays, p_1 and p_2 the work done by an electron in escaping from the atom and getting through the surface layer of the metal (p_2 corresponds to the contact potential). If the electrons are generated by monochromatic rays, they must be composed of distinct groups with perfectly definite velocities corresponding to different atomic levels—that is, to different values of the work p_1 . Measuring in some way or another the velocity of the electrons and taking account of the work p_1 and p_2 , we can determine the frequency ν .

The velocity of the secondary electrons can be measured by deflecting them in a given magnetic field. In this method, however, out of the whole mass of electrons streaming from the metal we must take a very narrow pencil; therefore, in the case of light elements, where the total intensity of the secondary current is very small, we can hardly expect to find a measurable effect in this way.

The method of a longitudinal electric field, stopping the electrons which stream from the illuminated plate of a plane condenser, is also inapplicable. If these electrons had the same velocity directed at random with respect to the plate, they would be stopped to a different amount depending upon the normal component of the velocity, the component parallel to the plate, *i. e.* perpendicular to the field, being unaffected by the latter. This corresponds to a parabolic shape of the curve secondary current-stopping potential.

In case of several different velocities we should get a composite curve, which it is practically impossible to analyse into the component parabolas, and thus draw any information about the corresponding groups of secondary electrons.

These shortcomings of the electrostatic method can be easily avoided if, instead of a *plane* condenser, usually adopted in experiments of this kind, we take a *spherical* one. When the inner sphere is illuminated by the rays of frequency ν , it emits secondary electrons in different directions but with the same initial velocities v . In radial electric field the electrons will move along any curve of second order and will reach the outer sphere as they move away from perihelion. When the retarding potential eV reaches the value nearly equal to their initial energy, only then will the electrons all at once be stopped and driven back to the inside sphere (this may be easily shown using the equations of motion of the electron in radial field). Therefore, electrons of the same group, that is of the same initial velocity, will be stopped at the same time that the potential difference exceeds the critical value V , determined by the relation $Ve = \frac{1}{2}mv^2$. This will correspond to a very marked drop of the secondary current on the curve current-potential.

I have used this method to determine the velocities of the secondary electrons. A similar method was used by Richardson and Compton for measurements of velocities of photoelectrons*. They illuminated by ultra-violet light the centre of a small *plate* placed inside the sphere. Then all electrons starting from the centre of the sphere moved approximately against the lines of force, and all were stopped by the field in spite of the difference in direction of their initial velocities. The advantage of the use of a *spherical condenser* consists in the fact that in this case it is not necessary to have a very small illuminated area. This is essential in the case of illumination by X-rays, which we cannot bring to a focus. For instance, if the radii of the sphere are in the ratio of 1 : 10 and the retarding potential eV is equal to 0.99 of the kinetic energy of the electrons, then all the electrons with the initial velocity of any direction *still reach* the outer sphere. With further increase of field the current begins to drop. For the ratio of the radii 1 : 5 the current begins to drop when the retarding potential has reached the value $eV = 0.96 \times \frac{1}{2}mv^2$.

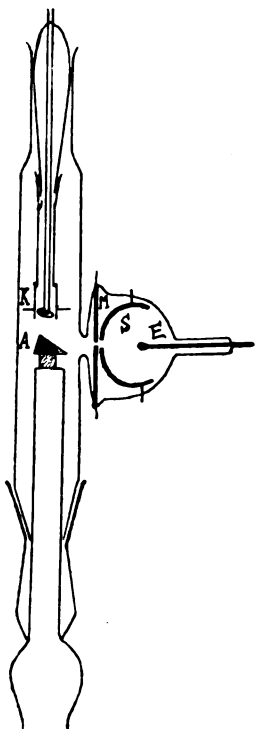
From these data it is easily seen that the illuminated inside sphere may have a comparatively great surface.

The apparatus is represented in fig. 1. The anticathode

* See Phil. Mag. October 1912.

A contained a bit of diamond which was bombarded by a pencil of (primary) cathode rays from a Coolidge cathode K.

Fig. 1.



The primary potential difference varied from 250 to 750 volts and the primary current from 30 to 80 milliamperes. X-rays from carbon (diamond) passed through a lead diaphragm M, and further through a hole in the external sphere, or rather hemisphere, S, falling on a thin zinc sphere E connected with a string electrometer. I measured the intensity of the secondary current i for different values of the (stopping) potential difference V between E and S. As the intensity of the primary current I was not quite constant, i was always replaced by the ratio $\frac{i}{I}$. The results obtained with

a primary potential difference of 750 volts are represented in fig. 2, the stopping potential V being taken as abscissa and the ratio $\frac{i}{I}$ as ordinate.

This curve shows three distinct drops: (1) a small one for $V=20-26$ volts; (2) another, also very small, for $V=115-123$ volts; and (3) a relatively strong drop for $V=248-252$ volts. This shows that among the secondary electrons excited by the Röntgen rays there are three distinct groups with perfectly definite velocities, corresponding to the above values of the stopping potential and wholly independent of the energy of the primary electrons. Whence we may conclude that, besides the continuous spectrum exciting secondary electrons of all the possible velocities (up to the limiting one corresponding to 750 volts), the diamond emits a characteristic radiation which is the cause of the electrons with definite velocities.

The numerical values obtained for these velocities may be interpreted as follows:—

Electrons with velocities corresponding to 243–252 volts are due to the K-line of carbon ejecting both outer and free electrons from zinc. The energy of one quantum of

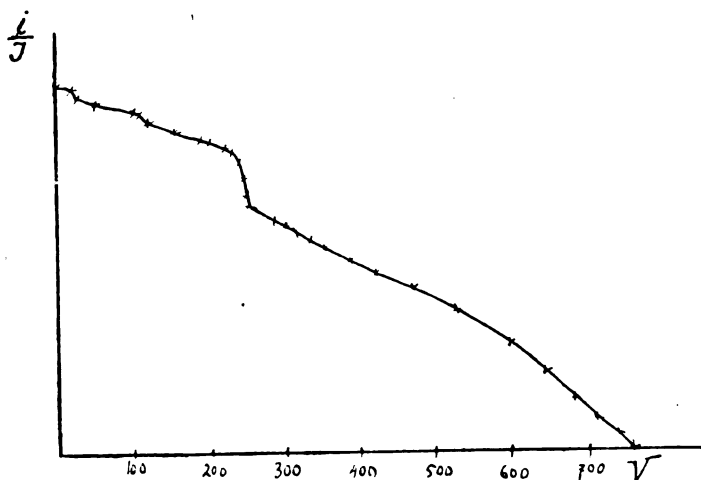
these rays is equivalent to 252 volts + the contact potential of zinc (1.2 volts), which corresponds to a wave-length $\lambda = 48.9 \text{ \AA}$. This result is certainly correct with respect to the order of magnitude; if we take Kurth's numbers for the limits of the K and L series of carbon (289 and 32.9 volts), then for the energy of the K-line we get

$$K = K_g - L_g = 289 - 32.9 = 256 \text{ volts.}$$

Richardson gives for $K_g = 286$ volts, what makes $K = 253$ volts, which almost exactly coincides with the above value.

The two other drops of the curve (fig. 2) may be explained in the following way:—The drop corresponding to 110–130

Fig. 2.



volts is due either to the ejection of electrons from the M group of zinc by the K-line of carbon, or of the free and outer electrons by the M-line of the same metal, which must be present as a line of fluorescence. Both explanations are correct with respect to the order of magnitude. Lastly, the small drop corresponding to 20–26 volts must be due to the ejection of electrons by extreme ultra-violet rays of carbon (the line 360 $\text{\AA}$, found by Millikan, corresponds to 27–28 volts).

Thus, measuring the velocities of the secondary electrons by means of a stopping electric field of spherical (radial) symmetry, it was possible to determine the wave-length of the carbon K-line, which proves to be 48.9 $\text{\AA}$. Although this method gives an accuracy to 1 per cent. only, it seems yet the only one which is used at present for the determination of wave-lengths in the interval considered.

The work is being continued.

Petrov, September 1923.

XXXVIII. *Notices respecting New Books.*

Relativity. A Systematic Treatment of Einstein's Theory. By J. RICE, M.A., Senior Lecturer in Physics in the University of Liverpool. Pp. xv + 397. London: Longmans, Green, & Co. 1923. Price 18s. net.)

THE theory of relativity has revolutionized the mental attitude of the physicist towards many of the concepts which he had been taught from his early days, and which have been used in the past as foundation stones upon which the grand structure of physical science has been reared. The question now arises as to what course should be adopted in instructing the coming generation of physicists. Should they be taught the old views until they have graduated and then be compelled at some subsequent time to readjust their point of view? Should they be allowed to study mathematics and physics with the belief at the back of their minds that the new knowledge has dealt a death-blow to all that they are supposed to be learning?

It is such questions as these which the author suggests in his preface. He believes that the young student should make as early an acquaintanceship as possible with the theory, so that he may know exactly to what extent the principles of physical science have been modified by the theory. This volume is therefore written primarily for the science undergraduate to enable him to adapt his mind to the new ideas as he pursues the normal University Courses.

This explains the order in which the subject is here treated, an order which corresponds neither to that usually adopted in works on the subject nor to the historical order of development. After a general introduction, in which the paradoxes into which the older views may lead us are considered, and in which the concepts of space, time, simultaneity, &c. are discussed, the modifications in kinematics and dynamics required by the theory are discussed. This is followed by a discussion from the relativity viewpoint of Maxwell's equations, introducing the Lorentz transformations and Minkowski's concept of a "space-time." A systematic treatment of tensor analysis follows, and this is used for the formulation of differential equations of the electromagnetic field and of the dynamics of continuous media which are compatible with the restricted theory of relativity.

The second part of the book deals with the generalized theory, the principle of equivalence, and the law of gravitation. The necessary extensions in the tensor analysis required for these developments are deduced. In the third part the notion of parallel displacement is introduced, and an account given of the extensions of Einstein's theory by Weyl and Eddington, with a view to deriving a mathematical theory of the electromagnetic field as well as of gravitation. The speculations of de Sitter and Einstein with regard to the finiteness of the Universe are also discussed.

The author has drawn largely upon the works of Weyl and Eddington, and there are no novel features in the mathematical exposition which call for comment. More use might with advantage have been made of the tensor-densities, employed extensively by Weyl. Care has been taken to point out any traps in the analysis into which the unwary may easily fall.

Whilst to those who are familiar with the relativity conceptions the order of treatment followed by Weyl and Eddington is to be preferred, the author is to be commended for this attempt to develop the theory in a manner which can be assimilated by the student along with his other studies. The treatment is carried further than would be necessary for a degree examination, but it is desirable that the discussion of the deductions from the theory should be complete. The student will thus be able, if necessary, to pursue the subject further in his post-graduate studies.

A Treatise on the Theory of Bessel Functions. By G. N. WATSON, Sc.D., F.R.S. (Cambridge University Press. 804 pages. Price 70s. net.)

BESSEL, Neumann, and other related functions investigated in this volume have generally arisen from the solutions of problems in astronomy and physics. Hitherto many of the methods employed may be said to be lacking in rigour, but to the mathematical physicist this want has in no way invalidated the formulæ and numerical results required for the problems in question.

"However important it may be to maintain a uniformly high standard in pure mathematics, the physicist may occasionally do well to rest content with arguments which are fairly satisfactory and conclusive from his point of view."

By his contributions to the theory of Bessel functions, many of which are incorporated in this volume, the author has added considerably to the literature of this subject. He has at the same time given a wealth of results, which are of practical application in physical problems and in the construction of tables of these functions. Of especial importance in this connexion are the chapters on the zeros of Bessel functions, Bessel functions of large order, and Neumann and Kapteyn Series.

The formula for the smallest zero of the Bessel function of high order ν may be compared with that given independently by Emde, viz.:

$$x_1 = \nu + 1.8568 \nu^{\frac{1}{2}} + 1.149 \nu^{-\frac{1}{2}}.$$

Similar series for the first ten zeros have been computed and employed in the calculation of tables similar to those of Bourget.

For functions of nearly equal order and argument, Prof. J. W. Nicholson's formula, involving $J_{\pm\frac{1}{2}}$, is

$$J_\nu(x) \sim \frac{1}{3} \left(\frac{2a}{x} \right)^{\frac{1}{2}} \left\{ J_{-\frac{1}{2}} + J_{\frac{1}{2}} \right\},$$

α being written for $x - \nu$, and the argument of $J_{\pm\frac{1}{2}}$, $\frac{1}{2}(2\alpha)^2/x^{\frac{1}{2}}$. The author has discovered similar expressions for $J_{\nu}(x)$ and $Y_{\nu}(x)$, with an upper limit less than $24/\nu$ for the errors involved, from a consideration of the work of Debye. In this, as in so many other examples, the actual errors are considerably less than those indicated above.

In the study of this subject some confusion has arisen from the introduction of a variety of Bessel functions of the second kind. Prof. Watson rightly upholds the view that Weber's function $Y_n(x)$ should be regarded as the standard function of this type.

Not the least valuable feature of the volume is the extensive collection of tables of Bessel functions, with the detailed chapter on their tabulation; tables of the J, Y, H, I, and K functions of zero and unit order, with J, Y, and H of order $\frac{1}{2}$; J functions of higher integral and half odd integral order, with Fresnel's integrals; functions of equal order and argument and the first forty zeros of J_n and Y_n . In the bibliography the author has considerably supplemented that of Nielsen in his *Cylinderfunktionen*.

These brief references convey a very inadequate idea of the contents of this volume, which includes all the more important advances made in recent years. Previous to the publication of this work, many of the most valuable contributions could only be found in scientific and mathematical journals and in the proceedings and transactions of Societies. Prof. Watson has succeeded in keeping pace with the rapid growth of Bessel function literature, and students of both pure and applied mathematics have cause to be grateful to him for devoting an immense amount of labour in making these theoretical and practical results conveniently accessible.

His treatise will long remain the standard work of reference on Bessel functions, and worthily maintains the high traditions of excellence of the Cambridge University Mathematical Series.

An Introduction to the Study of Alternating Currents.

By Dr. A. E. CLAYTON. (Longmans. 10s. 6d. net.)

DR. CLAYTON has undertaken the task of writing a textbook suitable for the electrical engineer whose mathematical equipment is not too extensive. The work before us can only be commended very strongly, as being fully in accord with the author's purpose. He avoids, at one and the same time, the temptation to overload the subject with long proofs of an analytical nature and the more insidious temptation, to an engineer, to accept somewhat loose reasoning by analogy as equivalent to real demonstration. We are not able to find any omission from the work which calls for attention, and the author has been singularly successful in incorporating into his scheme all the fundamental ideas which are

really vital to the student. We can give the work unqualified commendation, with the suggestion that it should find a place in the electrical library of every college of engineering.

It is, on the whole, conspicuously free from errors, and the publishers may be congratulated on the manner in which it has been produced.

The Atom and the Bohr Theory of its Structure. By H. A.

KRAMERS and H. HOLST. (London: Gyldendal. 10s. 6d. net.)

THIS work should find a good audience. The mathematical theory underlying current views of atomic structure is entirely suppressed, and the authors professedly set out to give an account of the actual facts known concerning the atom, and the various speculations now in existence, made at the School of Physics which Prof. Bohr has founded in so remarkable a manner at Copenhagen. We regard the existence of this school as being perhaps the second great achievement of Prof. Bohr.

Perhaps it is not possible, in a work of this kind, to make it quite clear to the reader which of the necessarily dogmatic statements are statements of fact, and which are quotations from current speculation, and we must not chide the writers of an excellent work for leaving the reader so often in the position of being unable to decide. A developing theory must contain much pure speculative matter to which no mathematical analysis can yet be applied, and the Bohr theory at the present day is notably one of this type. The writers are themselves very effective members of the school, full of enthusiasm, and able to write in a vivid style. Sometimes a curious note appears, which seems to imply that the theory has made a hard fight for acceptance, and we get a mental picture of Prof. Bohr with his back to the wall, repelling all assaults. This surely does not correspond to history, for the instantaneous general acceptance of the theory was, in fact, a very remarkable and unusual event.

Sir Ernest Rutherford contributes a foreword to the volume, which should be in the library of all those who are interested to know the precise position of thought in the great Danish School of Atomic Theory.

The Theory of Experimental Electricity. By W. C. D. WHETHAM. (Cambridge University Press, 1923. 12s. 6d. net.) Third Edition.

THE first two editions of this work were excellent, and did not leave much scope for alterations, except those called for by the development of electrical research in new directions. Such alterations as were necessary, however, have been made, and there are considerable additions. The author does not intend to give any comprehensive survey of the vast domain of electrical science as it exists to-day, with all its adjuncts such as the structure of atoms, theory of spectra, and so forth. He has wisely confined himself to the original scheme of the first edition, which was to incorporate the substance of a set of lectures into a per-

manent record of the fundamental principles underlying the usual electrical measurements made in the laboratory by the University student reading for Honours in Physics. The subjects thus treated comprise electrostatics, magnetism, the electric current and induction of currents, thermo-electricity and electrolysis, electric waves, conduction through gases, and radioactivity.

The treatment is lucid and the book is very pleasant to read, and this edition, like its predecessors, will certainly find its way into most electrical laboratories and libraries. As regards its form, we only recall that it is a member of the Cambridge Physical Series.

Clerk Maxwell's Electromagnetic Theory (The Rede Lecture for 1923). By H. A. LORENTZ. (Cambridge University Press, 1923. 1s. 6d. net.)

PROF. LORENTZ has paid a fine compliment to English physics by choosing, as the subject of his Rede lecture, the work of James Clerk Maxwell. Lorentz and Larmor developed the work of Maxwell, in its extension to moving media, to the point where it became clear that Maxwell's equations were invariant for uniform motion of the axes of reference. They did not, it is true, apply the simple alternative postulate of Einstein—that no effect of the earth's motion must be looked for,—but they provided the inspiration and analysis which rendered it possible to make this, their deduction, the actual starting-point. Prof. Lorentz sees Maxwell as the pioneer. His account of his work is sympathetic and of profound insight. Prof. Lorentz is well-known, and even loved among English physicists, for his gifts of humour and of understanding, which cannot hide the spark which fired the torch of all recent progress in electron theory and relativity theory. We can only congratulate the University of Cambridge on its choice of a Rede Lecturer and Prof. Lorentz on his lecture.

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. By DR. J. W. MELLOR. (Longmans, Green & Co.) Vol. III., 63s. net; Vol. IV., 63s. net.

VOL. III.—The author in this volume takes up the chemistry of Copper, Silver, Gold, and the Alkaline earths. The monumental character of the work is fully maintained: it is very difficult to find any piece of exact knowledge or interesting speculation which is not referred to with an appropriate reference. The author's historical references excite our admiration—for example, the history of Copper begins with Tubal Cain, 3870 B.C., Job, and Deuteronomy. The earliest specimen of bronze from Medun is chronicled as of date 3700 B.C., with its composition as percentages of tin, copper, and arsenic.

These serve only as examples of the thoroughness of the work. It is almost impossible, in a reasonable time, to count the number of references to the literature of any single element dealt with, or to estimate the amount of research into sources of information which the present account has demanded. The author sets a

model which all future encyclopædias will find a difficulty in imitating. But this feature continues: we dismiss the element Copper, and come upon a similar literature of all its known compounds. Then we turn to Silver, and so on.

In fact, this work is undoubtedly the indispensable reference book for every chemical library. Like the earlier volumes, in a sense, it certainly is; but as the work grows, the author's sense of thoroughness seems to grow with it. The author writes as a chemist, but it is certainly difficult to find any phenomenon of interest to a physicist, who is not also a chemist, which does not receive an adequate mention and discussion. Not even a book of tables is likely to be necessary to the possessor of these volumes, whether he be a physicist, chemist, or engineer. Even the spectroscopist can find the leading wave-lengths of the absorption bands. The whole work is a monumental record of observation and chemical theory, and seems to displace the whole literature of the subject, as at present known in scattered publications in various languages.

VOL. IV.—This volume deals with Radium and Actinium families, Beryllium, Magnesium, Zinc, Cadmium, and Mercury. The treatment is equally exhaustive, and begins with a chapter, of a general kind, on the structure of matter, and the various physical phenomena which have contributed to its elucidation. The second chapter takes up the general question of radioactivity, and gives a very satisfactory account of the chain of products from Radium to Lead. There follows a chapter on the general architecture of the atom, and then the author settles down once more to the more chemical side of his subject, with the whole literature of Beryllium.

Dr. Mellor is doing, for Chemistry, a task which no author has ever even attempted to do for any other branch of science, except perhaps Kayser, in his *Handbook of Spectroscopy*. But this is on a scale altogether different, as is the subject-matter itself. The manner in which it is being done is beyond criticism, except that perhaps it should not be called a treatise, but an encyclopædia. While we wish the author all possible speed with the succeeding volumes, we may well wonder whether his task can ever reach its end in the lifetime of one man.

Bibliographical History of Electricity and Magnetism, chronologically arranged. By Dr. P. F. MOTTELAY. (Charles Griffin & Co., Ltd., 1922. 42s. net.)

This work is described as an account of researches into the domain of the early sciences, especially from the period of the revival of scholasticism, with biographical and other accounts of the most distinguished natural philosophers throughout the middle ages. In actual fact, the author's claim, here made, is a very modest one, for the work contains much more, and is a worthy memorial of a lifetime spent in collating all available information from unexpected and quite new sources. The sad death of the author just at the close of his work is referred to in a touching

manner by Sir Richard Glazebrook in a foreword he has written for the volume, which was originally dedicated to Lord Kelvin.

The account begins at B.C. 2637, when the Emperor of China used a compass to direct his troops, and ends with Faraday in 1821. We have all quotations from the early Greeks, even Homer, which can bear on a possible knowledge of the compass—every known detail regarding the magnet and the views held concerning it.

The most exhaustive tests a reviewer can make seem to show that nothing is omitted.

The late Prof. Silvanus Thompson writes an introduction, commending the work not only for what it contains, but for the spirit which permeates every page—the spirit of appreciation of the work of those early pioneers who have created the subject as it exists to-day. To find just what any author has ever had to say about Electricity or Magnetism, it is only necessary to refer to these pages. Priority questions can be settled out of hand, with the assurance that the last word has been said.

We can only commend the work very strongly as an indispensable work of reference for any library designed to help either the worker or the student of the literature dealing with electrical science. The publishers are to be congratulated on its form.

Advanced Practical Physics for Students. By B. L. WORSNOP and H. J. FLINT. (Methuen. 21s. net.)

THE subject-matter of this work, regarded as an effective laboratory course for Students for Honours in the Universities, is in many respects ideal, and constitutes a great improvement on the courses which are contained in most existing works. The suggested experiments do appear to be suitable for stimulating the imagination of the student, and for giving him a vivid feeling of progress. They can only have been designed, in the sequence here presented, by those who have the essentials of teaching at heart.

While the work can be recommended with confidence, we may perhaps remark that the authors have not always been careful enough to avoid expressions of a slipshod nature, and even modes of statement which defy the ordinary rules of English grammar. Such errors can easily be corrected in a later edition, and seem to imply a somewhat hurried revision of the proofs. We wish the work every success, and a consequent early appearance in a form which is more pleasing to the æsthetic sense which physicists, like others, have.

Méthodes de calcul différentiel et leurs applications. By M. M. G. RICCI and T. LEVI-CIVITA. (Paris: Librairie Scientifique A. Blanchard, 1923. 9 francs.)

THIS memoir meets a need which is much felt in English mathematics. At one time it appeared in the *Mathematische Annalen*. The present volume is a somewhat tardy reprint, in French. In a real sense, it forms the ultimate basis of

the mathematical developments of Einstein's theory. It is now a matter of common knowledge that Prof. Levi-Civita is one of the outstanding authorities on tensor geometry, whose work so long escaped recognition.

We do not enter into detail regarding the contents of this small volume. They are expressed in the concise and elegant form to which the French language so readily lends itself. The work deserves complete commendation, and, if only as a page in the history of more recent developments, should be on the shelves of every library of physics or of differential geometry.

The Structure of the Atom. By DR. N. R. CAMPBELL.

(Cambridge University Press. 10s. net.)

THIS work is another of the supplementary chapters to the author's treatise on modern Electrical Theory, and is to be regarded as Chapter XVII. of that Treatise. The author's object is to help students who have taken the usual courses and are now in a position to get into touch with research. This work, like the other supplementary chapters, will fulfil that need by raising all the problems in which progress is now being made in regard to atomic structure, and by indicating the kind of method of attack which will most probably be successful in each instance.

At the same time, it is not possible to say that the very great standard of excellence of the original Treatise has been maintained. Signs of careless writing are numerous, and the MS. has clearly not been sufficiently revised in some places. The author is clearly aware that errors may exist, and apologizes for them with an explanation of the real difficulty which exists in constructing a connected story grouped about a few fundamental conceptions.

The author also refers to the difficulty of ascribing the names of original authors to particular facts or theorems elucidated by many workers, and raises a claim for more prominence of earlier authors who laid the foundations of the structure which Rutherford and Bohr have raised. While agreeing with him, we would point out that he has not applied the principle sufficiently fully. Authors of more recent date whom one naturally looks for are not always referred to at all, even when unquestionably the originators. This is equivalent to saying that the author has not always used the best sources for his information, and has tended to restrict himself to the writings, for example, of Sommerfeld, Bohr, and others, who, while contributing much, have naturally worked on special lines. Much important work by several writers in this Magazine, in the Proceedings of the Royal Society, and elsewhere, has more claim to attention than some of the highly speculative work included.

But we must not emphasize these points, for the author expresses his difficulty in obtaining collaborators who were able to help. He has produced a very readable account in a vivid style. What we have referred to as careless writing could easily be corrected in a new edition, which should be called for in due course.

XXXIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

Continued from p. 256.

December 5th, 1923.—Proc. A. C. Seward, Sc.D., F.R.S., President and, afterwards, Dr. G. T. Prior, F.R.S., F.G.S., in the Chair.

THE following communications were read:—

1. 'The Geology of the Northern Border of Dartmoor, between Whiddon Down and Butterdon Down.' By Charles William Osman, M.Inst.C.E., F.G.S.

The Lower Carboniferous rocks between the above points, a distance of about $4\frac{1}{2}$ miles, are described, and it is shown that these rocks may (as in the Okehampton border-district) be divided into a Lower Aluminous and a Calcareous Series, and that in this district the Lower Aluminous Series may be subdivided into two zones: the Lower, characterized by the abundance of pyrites; and above this, a zone in which chialstolite is found. The Calcareous Series commences with grey shales above the Lower Aluminous Series, without any physical feature, and contains a volcanic band, generally in a fragmentary condition, mixed with ash, slate, and other fragments, and impregnated with chert; but, at East Underdown, the rock is more solid, and consists of perthitic orthoclase-phenocrysts in a ground-mass of tufted albite-oligoclase, and is a quartzless keratophyre. The author endeavours to show that the corresponding mixed igneous rocks of the North-Western Dartmoor border, which have been variously described as 'trappean rocks', 'metamorphosed tuffs and trachytes', and 'dark igneous rocks', are altered keratophyres.

Above the volcanic band are two limestone-areas: one on the west, near Whiddon Down, and, separated by quartzose rocks, another limestone-area at Drewsteignton. The eastern ends of both these areas are cut by faults with crush, and show a limuritic change of contact-alteration; while the area east of Drewsteignton shows a secondary crush and shearing, producing a hornblende alteration imposed on the limuritic one. Throughout the length of border considered, the top of the Calcareous Series is formed of grey shales, with hard rock-bands which pass upwards into the Upper Aluminous Series.

The granite south of the Carboniferous border-rocks shows three separate intrusions. These are all from the same magma, but there are sufficient differences to separate them. The first, or great intrusion, is the country-rock granite G, with large orthoclase-phenocrysts measuring up to 7 inches in length, and disseminated tourmaline in the coarse ground-mass: this is generally much decomposed and crushed. The second intrusion, or G1 granite, broke up the country-rock (G) granite, and occurs as large dykes, and sills overlying the G granite. It has fewer and smaller orthoclase-phenocrysts, larger plagioclase-crystals, and may be

described as a cordierite-biotite-granite. The third, or fine granite (G 2) intrusion, occurs not only in smaller veins and sills, but also in a large marginal intrusion along a width of border of about $2\frac{1}{2}$ miles. This granite overlies both the G and G 1 granites on the south-east of the area described.

2. 'The Geology of Southern Guernsey.' By Donald John Farquharson, M.Sc., F.G.S.

With the possible exception of some dykes of doubtful Palæozoic age, the whole of Guernsey consists of pre-Cambrian rocks—gneisses and schists in the south; unfossiliferous shales and grits at Pleinmont; and a series of intrusions in the north, which range from hornblende-gabbro through diorites and tonalites to granites with their accompanying dykes. These dykes not only pierce the last-named suite, but also the gneisses and grits of the south.

Prof. T. G. Bonney & the Rev. E. Hill were the first to study Guernsey geology on modern lines, and Mr. J. Parkinson has worked on the differentiation-suite of the north.

The succession appears to be as follows:—

Palæozoic.....	Dykes (dolerite, quartz, lamprophyre, etc.).
Pre-Cambrian	C { Dykes (basic and acid). Granite (of Cobo). Differentiation-suite.
	B Pleinmont Shale and Grit.
	A { Diorite-gneiss. Dykes (now metamorphosed). Granite-gneiss. Jerbouurg Schists.

Group A consists of dynamically altered, foliated rocks, with a foliation ranging from north-west and south-east to north-east and south-west. The granite-gneisses are mostly porphyritic, and are characterized by abundant microcline. The dioritic gneisses, which verge on tonalites, occur at Divette and from Rocquaine to Torteval; the type characteristic of the last-named locality was first observed by the Rev. E. Hill near St. Andrew's brickfield, in 1884.

The Pleinmont Shale, first observed by Dr. G. H. Plymen, occurs more widely than was previously supposed, and is younger than the gneisses. It is followed by normal diorites and granites, which prevail in the north; but dykes of this set, mostly of dolerite, are very abundant on the southern coast. Some sill-like intrusions of a coarser dioritic rock occur in the gneiss of the eastern coast, and may be assigned to the differentiation-suite; this applies also to the pierite of Bon Repos, noted by Bonney & Hill. A spherulitic felsite occurs near Câtél, but its relations are obscure.

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XL. Dimensional Analysis.
*By NORMAN CAMPBELL, Sc.D.**

Summary.—A re-examination is made of the physical assumptions underlying dimensional analysis, and suggestions are offered of a method of employing dimensional arguments which is less liable to error than those at present in vogue. The final conclusion is stated in §10, the method advocated (which is not new, but the oldest method of all) in §4.

Incidentally some arguments by Jeans and Einstein, which seem to have been accepted as valid, are discussed. It is concluded that the former, while formally valid, are insignificant and do not really involve the conception of dimensions; and that the latter are completely fallacious.

§1. **I**N 1915 the late Lord Rayleigh wrote †:—“I have often been impressed by the scanty attention paid even by original workers in physics to the great principle of similitude.” Nobody could make a similar statement to-day. During the past nine years, starting with Buckingham’s work ‡, there has been a copious stream of papers, and even books, dealing generally with the principle §, while applications of it are to be found in almost every volume of every

* Communicated by the Author.

† Rayleigh (3rd Baron), ‘Nature,’ xcv. p. 66 (1915).

‡ E. Buckingham, *Phys. Rev.* iv. p. 345 (1914).

§ *E.g.* Buckingham, *loc. cit.*; C. Runge, *Phys. Zeit.* xvii. p. 202 (1916); Ehrenfert-Afanassjewa, *Math. Ann.* lxxvii. (1916); N. R. Campbell, ‘Physics: The Elements,’ Camb. Univ. Press, 1920, chs. xiv., xv.; P. W. Bridgman, ‘Dimensional Analysis,’ Yale Univ. Press (1922); F. London, *Phys. Zeit.* xxiii. p. 262 (1922); J. Wallot, *Zeit. f. Phys.* x. p. 329 (1922).

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physical journal. Yet I do not think that Rayleigh, if he were still with us, would be entirely satisfied with the change. He would probably regret the tendency to expound the principle with great formal generality and considerable mathematical elaboration which, initiated by Buckingham, has led finally to the imposing title of "dimensional analysis"; and he would certainly regret the absurd perversions and erroneous applications of the principle which have been seriously propounded. These two things are closely associated. Rayleigh in his use of the principle was always careful to insist on the particular physical assumptions involved rather than on the general logical deduction; and it is almost certainly the obscuring of the former by an undue and entirely unnecessary elaboration of the latter that has led so many astray.

Accordingly, although I have little new to add to a discussion which is already sufficiently voluminous, it may not be waste of space to draw attention once more to the physical rather than the logical principles upon which "dimensional analysis" depends, and, reversing recent developments, to consider the manner in which it can be applied with the least elaboration and therefore with the least probability of error.

§2. Physical assumptions are introduced into dimensional arguments at three stages:—

(1) When it is decided that the systems to which the argument is to be applied are physically similar, and have throughout the same no-dimensional magnitudes.

(2) When it is decided what are the magnitudes which determine the process discussed.

(3) When definite dimensions are assigned to these magnitudes.

In most treatments of the subject, it is the second question which receives most attention: the first is often barely mentioned, and the third is answered simply by the exhibition of a list of all the principal magnitudes together with their dimensions. This last procedure I believe to be, if not actually erroneous, highly misleading; the delusion that it is necessary for the purpose of the argument to assign to all magnitudes fixed dimensions in terms of certain fixed fundamental units is the cause of most of the difficulties that have arisen. Accordingly, we shall consider the third question first.

When we say that a magnitude has certain dimensions we mean that it is involved in some numerical law having a certain form or—to be more accurate,—if we do not mean

this, we are merely making an arbitrary statement which is neither physically true or physically untrue, and which cannot therefore be the basis of any physical argument*. Now many magnitudes are involved in laws of more than one form, and with more than one set of other magnitudes; accordingly, it is possible to assign to such magnitudes more than one set of dimensions in terms of more than one set of other magnitudes. The general practice is to select one of the many possibilities, and to state once and for all that, in virtue of one particular law in which the magnitude is involved, it has certain dimensions in terms of certain other magnitudes. This method of procedure can be justified † to this extent, that it is possible by pursuing it with great care and elaboration to found on it valid dimensional arguments; but it is certainly not the natural or the most convenient procedure. The only laws that can be relevant to a consideration of the behaviour of any system are the laws that determine that behaviour; and, consequently, the only dimensions that are relevant are those fixed by these laws.

Surely this is obvious enough; but if it is, how do such questions as whether temperature has or has not the dimensions of energy come to be debated? ‡ The answer is clear. The assignment of the dimensions of energy is determined by the laws of a perfect gas or by theories, such as molecular theory, which explains those laws. If these laws, or other laws based on these theories, are relevant to the process under consideration, temperature should be given

* I am not sure how far the truth of this statement is generally recognized. It is, of course, implicitly involved in all discussions of the matter that are not utterly ridiculous, but it is not often stated explicitly. But it is difficult to see how the supposed difficulties mentioned below could ever have arisen if it had always been borne in mind. In case the truth of the statement is not immediately familiar, it may be mentioned that it is discussed at great length in my 'Physics' (*loc. cit.*).

† It cannot be justified by considering how the unit of the magnitude would have to be changed if that of other magnitudes were changed, for there is no compulsion whatever to change units so as to preserve the formal constants in laws. If the inch were substituted for the centimetre as the unit of length, there is no compelling reason why the cubic inch rather than the cubic foot should be taken as the unit of volume; indeed, since the cubic centimetre is *not* now the unit of volume, but the volume of unit mass of water, there is no reason why the unit of volume should be changed at all. No law can be stated in terms of choices of units which are always, and must always remain, wholly arbitrary.

‡ The question seems first to have been put by D. Riabouchinsky in connexion with Rayleigh's argument based on Boussinesq's equation. Rayleigh's answer ('Nature,' xcv. p. 644 (1915)) was evasive. The matter has been discussed by (amongst others) Bridgman, 'Dimensional Analysis,' and Wallot (*loc. cit.*).

the dimensions of energy ; if not, it should not. Boussinesq's equation depends neither on Boyle's and Gay-Lussac's laws, nor on molecular theory ; Rayleigh was therefore right to treat temperature as a fundamental magnitude, or rather simply as a magnitude of which the dimensions were connected in a certain manner with those of specific heat and thermal conductivity. To have given temperature the dimensions of energy would have been to introduce considerations altogether irrelevant and therefore, as Riabouchinsky pointed out, to make the problem indeterminate. On the other hand, Einstein *, in a paper to which further reference will be made, was right to give temperature the dimensions of energy, because the assumption that the temperature is proportional to the mean energy of a molecule is inherent in his argument.

In the same manner, electric charge is to be given its electrostatic or electromagnetic dimensions according to the laws which are relevant to the problem. If charges enter only because they exert forces in accordance with Coulomb's law, then electrostatic dimensions must be used ; if they enter because a moving charge produces a magnetic field, electromagnetic dimensions should be used. If, in any problem, both electrostatic and electromagnetic forces are involved, two magnitudes must be introduced into any dimensional argument, one having one set of dimensions, the other the other.

But the removal of these difficulties is only incidental to my main purpose, which is to insist that the dimensions of the relevant magnitudes cannot be assigned, and, consequently, the dimensional argument cannot be applied, until we know exactly what are the laws determining the process that is under consideration. It is not sufficient to know what magnitudes are involved—if, indeed, it were possible to know that without knowing what laws are involved ; we must know the laws in order that the dimensions may be fitly assigned. It is true that there are certain magnitudes—liquid viscosity is one of them—which are involved in only one form of law known at present, the law namely by means of which they are defined ; but it is not permissible in all circumstances to conclude that they must have the dimensions appropriate to that law, for it is possible that other laws exist and may some day be found in which they occur. Such a conclusion is only permissible when there is strong reason to believe that it is the law by means of which they

* *Ann. d. Phys.* xxxv. p. 686 (1911).

were originally defined which is actually operative in the problem discussed.

§3. Our discussion of the third question, what dimensions are to be assigned to the magnitudes, makes the second, what magnitudes are relevant, insignificant. For of course if we know all the laws determining the process, we know the magnitudes involved in them. Let us pass then to the first, the assumption that the systems compared are physically similar.

In the simplest cases our knowledge is very direct. It is proposed to apply conclusions only to systems known to be geometrically similar, while all magnitudes other than geometrical are known to be the same throughout any one system and, consequently, necessarily similar as between two systems. This is the position in the argument applied to the simple pendulum or the acoustic resonator. The systems compared are geometrically similar, while there is for each system only one period of vibration and one value of gravity or of the velocity of sound. But few cases are so simple. Consider, for example, the familiar hydrodynamical argument, so widely used in model experiments on ships or aircraft. Here geometrical similarity is assumed, while the velocity of the model and the specific properties of the medium are the same throughout any one model; but the argument will not hold unless the forces are similar—that is to say, unless the ratio of the forces acting on two parts of a model is the same for corresponding parts of all models. But there are undoubtedly many forces acting on the model. What exactly is the foundation for this assumption of the similarity of the forces?

I think it can only be found—and this is my second main conclusion—in the form of the elementary laws which determine the motion. These laws are expressed by differential equations which, in the example taken, can be written down completely. If they could be solved by straightforward analysis a complete solution could be obtained, and there would be no need of the dimensional argument at all: that argument is merely a way partially to evade insuperable mathematical difficulties or practically impossible numerical labour. Now the mathematical process of integration corresponds to the physical process of addition; the addition of similar magnitudes belonging to two systems can only lead to magnitudes of the same kind belonging to those systems which are also similar. The argument which leads to a belief that the systems considered are similar in respect of all relevant magnitudes may therefore be stated thus. A certain

equation, involving certain magnitudes, is true of every element of each of the systems considered. (In our example the element is spatial; in others it is temporal, or, more rarely, defined by magnitudes of other kinds.) The elements of any one system are similar to corresponding elements of any other system in respect of all the magnitudes concerned in the equations; and consequently if, by integration or the summation of magnitudes characteristic of these elements, any relation is obtained true of magnitudes characteristic of the systems as wholes, these systems must also be similar in respect of these magnitudes. There is only one point in this argument to which any doubt can attach, namely the assumption that the integration of the equations will lead to a relation between magnitudes which, being of the kinds characteristic of the elements, are also characteristic of the whole system. Thus, in our example, it is not certain from a mere inspection of the fundamental differential equation that there will be any resistance to the motion of the body, determined by a constant velocity; integration might have led to the conclusion that the body would move in discontinuous jerks. Or—to take another example which may seem more plausible—it is not immediately obvious from the differential equation of the motion of the pendulum that the motion will be periodic and that the system will have a period. The conclusion is only justified by experimental knowledge that there is a relation of the type sought; it is here that assumption (2) of p. 482 enters in a way that is not an immediate consequence of assumptions (1) and (3).

§4. The conclusion that I want to enforce is that, in some of the problems to which dimensional arguments are applicable, the argument is only valid if the laws determining the behaviour of the system are completely known, and are actually expressible in the form of differential equations, the integration of which by purely mathematical processes would give a complete solution of the problem. This conclusion is not new; it seems to be advanced by Bridgman (*loc. cit.* p. 52), but its implications do not seem to be sufficiently recognized. For if the fundamental differential equation can be stated, all the elaboration of assigning dimensions to the magnitudes in terms of fixed fundamental units is unnecessary, and so is all the mathematical apparatus of Buckingham's Π theorem. The conclusions that it is permissible to draw follow directly from the meaning of similarity, and the identity of no-dimensional magnitudes for similar systems. Thus the fundamental hydrodynamical

differential equation for incompressible fluids is

$$\rho \frac{du}{dt} - \eta \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) u - \frac{\partial p}{\partial x} + X = 0, \text{ etc., } \quad (1)$$

where X is a force per unit volume. Consequently, if l is a length, the following combinations must be the same for all similar systems:

$$a = \frac{\rho ul}{tp}, \quad b = \frac{\eta}{\rho} \cdot \frac{t}{l^2}, \quad c = \frac{X \cdot l}{p} \dots \dots \dots (2)$$

The last of these is insignificant, for p means a force per unit area; it tells us nothing that we have not already stated in introducing p . But the first two are significant. If there is a steady state, independent of t , and defined by (1), t must not occur explicitly; the only time that enters must be that defined by the law

$$l = u \cdot t. \quad \dots \dots \dots (3)$$

Hence

$$a = \frac{\rho u^2}{p}, \quad b = \frac{\eta}{\rho ul}; \quad \dots \dots \dots (4)$$

and the law required must be expressible in the form that any function $f(a, b)$ is the same for all systems. This is the usual conclusion, attained without any explicit reference to particular dimensions; all that is required is the knowledge that all terms in an equation have the same dimensions, in the simple sense that they have the same numerical values for all similar systems. The dimensional argument appears to have been originally used by Fourier in this manner.

§5. The question now arises whether this example is typical. I maintain that it is typical; and that dimensional analysis, as that term is usually understood, can be validly and usefully employed only when we can write down a fundamental differential equation which (together possibly with other equations) determines the process in question, and which, if it could be integrated, would furnish a mathematically complete solution of the problem. Or since such a universal negative is difficult to prove, I would maintain more particularly that all the valid and useful applications of that analysis that have actually been made are valid and useful, only in so far as the assumptions on which the analysis is based are derived from the study of such a fundamental equation.

That statement could be justified completely only by a detailed examination of all the applications that have ever been made. Such an examination I do not propose to undertake; for strong evidence can be brought in favour of my

contention by the examination of classes rather than of individuals. The three classes into which applications of the "dimensional analysis" naturally fall are:—I. Those in which a result is proved which had not been proved before. II. Those in which a result is proved which had been proved before. III. Those in which the result is not proved, but is assumed to be known empirically, and conclusions are advanced concerning the premisses from which the empirically known result could be proved.

§6. I. Applications in this class are obviously useful if they are valid. All examples of it which I have discovered are valid; and they are all of the type considered in §4 above. In every case the fundamental differential equation was known before the application of dimensional analysis; it was not always known to be true, and so far as its truth was uncertain the result of the application was recognized to be uncertain; but—this is the point necessary for our purpose—the knowledge on which the use of the method here proposed could be based was available, if only in the form of an assumption. Of course, it is open to anyone to say that the knowledge was not used, and that dimensional analysis would have given the result without it; but the facts and the arguments here advanced surely throw the *onus probandi* on those who make such an assertion. The new knowledge attained by the use of dimensional arguments was either a partial solution of the fundamental equation, which had not been solved before, or, much more often, the extension (apart from numerical constants) of a result already attained by a complete solution of the equation in the simpler cases.

And here it is relevant to notice an example in which, by the method of §4, a correct and new result was obtained which was not obtainable (or at least was not obtained) by dimensional analysis"*. This example is the characteristic curve of a high vacuum electron current from a thermionic cathode. Langmuir† has shown that, if the electrodes are plane parallel or cylindrical concentric, the current density (σ) is connected with the voltage (V), the distance between the electrodes (l), and the mass and charge of the electron (ϵ, m) by the relation

$$\sigma = C \cdot \sqrt{\frac{\epsilon}{m}} \cdot \frac{1}{l^2} V^{3/2}, \quad (6)$$

where the constant C depends on the shape of the electrodes.

* Attention has already been drawn to this example in 'Nature,' ex. p. 10 (1922).

† Phys. Rev. ii. p. 450 (1913).

The form of this relation immediately suggests that it ought to be deducible by dimensional analysis; but if we proceed by Buckingham's method, putting

$$[\epsilon] = [M]^{1/2} [L]^{3/2} [T]^{-1},$$

$$[\sigma] = [M]^{1/2} [L]^{-1/2} [T]^{-2},$$

$$[V] = [M]^{1/2} [L]^{1/2} [T]^{-1},$$

we can only deduce

$$\sigma = C \cdot \frac{V^2}{\sqrt{l^3 m}} f\left(\frac{e}{Vl}\right). \quad (7)$$

But let us study the fundamental differential equation. It is

$$\frac{d^2 V}{dx^2} = 4\pi\rho, \quad (8)$$

with

$$\sigma = \rho v, \quad (9)$$

$$\frac{1}{2}mv^2 = eV. \quad (10)$$

By elimination we get

$$\sqrt{V} \frac{d^2 V}{dx^2} = 2\sqrt{2\pi} \cdot \sigma \sqrt{\frac{m}{e}}. \quad (11)$$

It follows immediately that if by integration we obtain a relation between V , the total potential between the electrodes, and l the total distance between them, measured (like x) parallel to the stream lines and to the lines of force, then it must be of the form

$$\frac{V^{3/2}}{l^2} = C \cdot \sigma \sqrt{\frac{m}{e}}, \quad (12)$$

which is (6).

The reason why the dimensional argument in Buckingham's form leads to an ambiguity is that there has been omitted from it an essential assumption, namely that the stream-lines and lines of force are identical. This assumption can be introduced ('Nature,' *loc. cit.*) by treating area (or volume) as a fundamental magnitude, in place of as a derived magnitude with dimensions L^2 (or L^3). But my contention is not that, given the right assumptions, formal "dimensional analysis" will not give the right result, but that it is impossible to be sure of making the right assumptions without examining the complete equations. In this instance it is impossible without examining the equations to realise that there are two lengths involved, parallel and perpendicular

to the stream-lines, and that, while similarity in respect of the former is required, similarity in respect of the latter is not.

§ 7. II. The purpose of applications in this class is often purely didactic; the examples are merely given to show how the argument might be applied in examples of class I. If given for that purpose, they are wholly unobjectionable, but for the original investigator, skilled in the tools of his trade, they are hardly useful. However, some writers, in giving such examples, appear to proceed beyond mere demonstration by example: they seem to imply that the fact that their methods lead to correct results shows that those methods are sound. Such an implication is, of course, objectionable in the highest degree; it is easy enough to prove a true conclusion (even from true premisses) by an unsound argument, when the true conclusion is already known. The true result proves nothing about the validity of the reasoning; that validity cannot be established by induction, but only by a thorough examination in the light of logical principles. Moreover, even if any evidence of the validity of certain methods were established by such methods, a highly dubitable assumption remains. It is one thing to choose the magnitudes on which a process depends and to assign to them the right dimensions, when the conclusion and an argument by which it can be deduced validly are already known; it is quite another thing, when the conclusion and the argument are not known. The exhibition of these trivial examples to show how easy is dimensional analysis, without a full discussion of the assumptions involved and the nature of the argument, is the cause of all the errors to which it has given rise; it cannot be too strongly deprecated.

Most of the previous proofs of examples in class II. depend on differential equations, and therefore could not in any circumstance offer evidence against the position here maintained. But there is one curious example to the contrary, the only one of the kind that I have discovered, which therefore needs a moment's attention.

It is Jeans' deduction*, quoted by Rayleigh (*loc. cit.*), of the proposition that, if the viscosity of a gas varies as T^n , the force between its molecules must vary as r^{-s} , where

$$s = \frac{2}{n - \frac{1}{2}} + 1. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The complete proof of this proposition, previously given by

* J. H. Jeans, 'Dynamical Theory of Gases,' Camb. Univ. Press, 1904, p. 275.

Jeans (*loc. cit.* p. 256), is not derived from a differential equation. True; but there is also no application of the principle of similarity. The essence of such analysis is the deduction of a relation between magnitudes $A, B, C, \dots$ from a relation between magnitudes a, b, c , A being of the same kind as a , but not being actually the same magnitude. If A and a are the very same magnitude, there is no question of similarity, which is the basis of "dimensional analysis," and which renders necessary a knowledge of the differential equation; there is identity. Now in this case of viscosity the equations from which we start, and which take the place of differential equations, involve the very same magnitudes as those between which the final conclusion is stated. The κ, m, C, μ involved in equations (582), (583), (584) (*loc. cit.*) are precisely the same magnitudes as those introduced in the "dimensional argument" on p. 275. The result given follows by the merest algebraic elimination; the mathematical apparatus necessary to obtain the result directly is an exact reproduction step by step of that involved in the "dimensional" argument. Dimensions are utterly irrelevant; given the equations, the result follows whatever the physical nature of the quantities involved in them.

§ 8. III. At first sight this class might appear to provide examples of the well-known procedure whereby, from the concordance between a known empirical law and a proposed theory, we prove the truth of the theory. And this view would be correct, if the premisses from which the empirical law is deduced were some definite theory. There are cases in which this condition seems to be fulfilled; and in all of them the theory is expressible in the form of a differential equation; it is shown that a partial solution of that equation by the method of § 4 leads to the empirical law. Such a procedure is perfectly correct; but in practice examples of this nature are not easy to distinguish from those of Class I.; the distinction depends upon whether the empirical law (which is not always quite certain) or the proposed theory is regarded as the more firmly established. But these are not the typical examples of Class III. In the typical examples, the premisses are not a definite theory, expressed in any kind of equation, but the mere assumption that the process considered depends wholly on magnitudes of the kind occurring in the empirical law. (See examples below.) Now this assumption is always highly precarious, for it is liable to be false if there is involved in the process any unknown universal constant; and laws such as these, of which, *ex hypothesi*, no theory is certainly established, are

just those most likely to involve such a constant. A simple example will make this matter clear. If we were ignorant of gravitation, we might argue that the period of a planet was to be explicable on some theory involving only a time and a length; for empirically the period depends on nothing but the radius. It is only when we recognize the universal constant of gravitation that we realize that an adequate theory must involve mass.

Further, it is not clear what such an argument could prove, even if it were valid; apparently it is suggested that an empirical law is confirmed if it can be shown to be a consequence of *every* reasonable theory. But we need not discuss this matter further; for actually all examples of this nature that I have found involve other fallacies, and since these fallacies bear out well my contention, two of them may be examined more closely.

§9. These examples are provided by the attempts of Einstein* and his imitators† to deduce relations between the specific properties of metals, such as the thermal conductivity, the melting-point, specific heat, and compressibility. In the paper mentioned Einstein gives three such deductions. The first is perfectly correct, and founded, like all correct deductions of this kind, on a differential equation in an earlier paper‡. If the argument here proves anything, it is that the same result would follow from regular arrangements of the atoms (similar in all substances) other than that assumed in the detailed calculation§. The second is either valueless, reducing to a variant of the Jeans example, or incorrect. The assumption made is that the natural frequency of the material depends only on the mass and distance apart of the atoms and on their mean energy at the melting-point (or other "corresponding state"), which is measured by the temperature. Now either (1) the natural frequency

* A. Einstein, *Ann. d. Phys.* xxxv. p. 686 (1911). I omit here all reference to Einstein's views about the numerical value of the "undetermined constant"; those have been dealt with elsewhere ('Physics,' pp. 427-429)—any objections which may be urged against them are independent of and additional to those with which we are here concerned.

† *E.g.*, L. Schiller, *Zeit. f. Phys.* v. p. 159 (1921).

‡ A. Einstein, *Ann. d. Phys.* xxxiv. p. 170 (1911).

§ It may be pointed out that, since the deduction is valid only if all metals are geometrically similar in the arrangement of their atoms, and since it is known now that they are not so similar, the dimensional argument shows that the formula deduced can be at best an approximation.

is the reciprocal of the time in which an atom, moving with the velocity corresponding to its mean kinetic energy, traverses the distance between two atoms, or (2) it is not. If (1), then the meaning of the quantities involved leads to algebraic equations between the very quantities with which the conclusion is concerned, the conclusion being reached by mere substitution and elimination; no assumption concerning similarity is made, and, on the other hand, nothing whatever is added by dimensional analysis to what may be proved by the most elementary mathematics. If (2), it must be assumed that, in all metals, all frequencies are similar to this frequency; there must be no forces producing velocities which are not similar to the velocities of thermal motion. This assumption is almost certainly incorrect. A false assumption concerning similarity has been made, because a fundamental differential equation was not present as a guide.

The third example relates thermal conductivity to mass and distance apart of the atoms, natural frequency, and temperature. Now Einstein has just proved that the experimentally known relation between thermal conductivity and temperature is inconsistent with classical mechanics. The only alternative known to classical mechanics is quantum mechanics (relativity is here irrelevant). On what grounds then can he be so certain that h is not to be included among the quantities on which the thermal conductivity depends? Yet if it is to be included, his conclusion does not follow. But there is an even more surprising assumption involved in his argument. The thermal conductivity means the energy transferred in unit time across unit area perpendicular to unit temperature gradient; on the other hand, temperature is taken to be proportional to the mean energy of a molecule. Energy therefore enters twice; the argument is not valid unless the two energies are similar—that is to say, it is not valid, unless in all substances under all conditions the energy flowing in times inversely proportional to the natural frequency is proportional to the mean energy of a molecule. But this condition can be attained only if a specified temperature gradient is maintained in each material at each mean temperature. Or the same objection may be put in another way which is closely connected with our observations on p. 484. In the process considered there are two laws involved, both involving temperature. One is the law of thermal conductivity, defining that magnitude, that the heat flow is proportional to the temperature gradient. The second is that the mean energy of a molecule is proportional to the

temperature. Since temperature is involved in two independent laws, it requires to be introduced twice, with two different dimensions, into the argument. Or, once again—these objections though differing in form all are equivalent,—an examination of the previous calculation shows that the fallacy enters because the atomic specific heat is taken as no-dimensional. It is so taken because it is (approximately) a universal constant. But, as has been insisted already, universal constants are not necessarily no-dimensional. Such are the fallacies into which even the greatest physicists may fall when they attempt to base dimensional arguments on anything but a complete and exhaustive statement of the laws determining the process they study.

§10. Our final conclusion then is this. Dimensional analysis is useful and valid only when the assumptions concerning the magnitudes involved and their dimensions are based on the inspection of equations expressing fully the numerical laws or theories by which the process under discussion is determined. If they are so based, then all the formalities which various writers have elaborated are useless; no fixed dimensions or fixed fundamental magnitudes need be introduced; all that is required is a sound appreciation of the meaning of similarity and a knowledge of the rule, which is one of its obvious consequences, that all terms in a numerical law have the same dimensions.

It is probable that, in all useful and valid cases, the fundamental numerical laws or theories are expressible in differential equations; and that the only significant result of dimensional analysis is the generalization, for cases in which those equations are mathematically intractable, of a result which can be established by full mathematical reasoning in simpler cases. It is possible that there are exceptions to this statement, though none have been discovered. In any case the errors that arise when dimensional arguments are based on anything but differential equations are so facile and so plausible that any argument not so based should be accepted only after the most careful scrutiny in the light, not of an elaborate statement of the formal logical process employed, but of the physical significance of the assumptions made.

XLl. Viscosities of Liquids experimentally correlated to Pendulum Dampings. By Prof. E. H. BARTON, *F.R.S.*, and H. M. BROWNING, *M.Sc., Ph.D., University College, Nottingham* *.

[Plate I.]

THE appearance of some of the exponentially-damped vibration traces obtained in the course of recent work † suggested the idea of producing such dampings by utilizing the viscosities of liquids. This seemed likely to give a simple illustration of the relations holding between viscosity and damping and possibly provide a method for the comparison of viscosities, if not for their actual determination.

For this purpose the pendulum in use carried (by brackets on its rod) a pair of planes dipping into the liquids whose viscosities were under test, and moving parallel to and at measured distances from the inner side of the vessel containing them. For the liquids, samples of glycerine were used with different water contents, their densities and temperatures being noted and therefore their viscosities calculable. On plotting graphs of the results these seemed to be consistent enough to justify the use of interpolation or extrapolation. By the latter the viscosity of a sample of oil was determined. The method therefore seems suitable for laboratory use and may perhaps be as accurate and more expeditious than some others. The apparatus could be modified so as to be suitable for viscosities as low as those of water.

Apparatus.—The photographic reproduction (Pl. I.) shows the apparatus used. One of the brackets and the dipping plates carried by it are seen towards the top of the lath and near the axis of suspension, because the corresponding tank was removed to show it. The other tank was left in position. The two tanks containing the liquids are adjustable to and from the lath so as to set by a pair of gauges the exact distance required between the moving plates dipping in the liquid and the fixed side of the tank near which they move.

The apparatus as shown is suitable for liquids like glycerine and oil, the viscosities of which range from 8 to 2 c.g.s. units. For much smaller viscosities, as that of water of the order 0.01 c.g.s. unit, the pendulum bob would be made lighter, the dipping plates larger and placed much lower on the lath. In this way the sensitiveness might be increased a hundred fold or more as desired. The board near the base

* Communicated by the Authors.

† Phil. Mag. vol. xlvi. pp. 399-406, Sept. 1923.

of the apparatus is drawn along by hand, timed by a metronome, and receives the traces of salt left by the pendulum.

Theory.—Let a lath and bob pendulum carry plane plates dipping into the viscous liquid at distance z from the plane sides of the tanks which contain it. Then we may write as the equation of motion for small oscillations

$$I \frac{d^2\theta}{dt^2} + C \frac{\eta}{z} \frac{d\theta}{dt} + G\theta = 0, \quad (1)$$

where I is the moment of inertia of the pendulum about its axis of suspension, C and G are constants for the pendulum, and η is the viscosity of the liquid, that of the air being neglected,

or
$$\frac{d^2\theta}{dt^2} + 2k \frac{d\theta}{dt} + p^2\theta = 0 \quad (2)$$

where $k = (C\eta/2Iz) + p\lambda_0/\pi$ and $p^2 = G/I$. . (3)

and λ_0 is the logarithmic decrement of the pendulum due to air only without any viscous liquids in use.

The solution may be written

$$\theta = e^{-kt} (A \cos qt + B \sin qt) \quad (4)$$

where $q^2 = p^2 - k^2 = p^2$ nearly (5)

and A and B are arbitrary constants depending on the initial conditions.

Hence the logarithmic decrement per half-period is given approximately by

$$\lambda = k\pi/p = \{C\eta\pi/2z\sqrt{(GI)}\} + \lambda_0 \quad (6)$$

or $\lambda - \lambda_0 \propto \eta/z$ (7)

Further, if the amplitude of the vibration is reduced to a half in n half-periods, we have

$$e^{-nk\pi/p} = \frac{1}{2} = e^{-n\lambda} \quad (8)$$

Thus for any given vibration, we have

$$\lambda = \frac{1}{n} \log_e 2 = \frac{0.69315}{n} \quad (9)$$

and n will be a useful experimental gauge for λ .

Experiments.—As the viscosity of the glycerine varies so

much with temperature and with its water content (which is spontaneously varying), it was necessary to take the density before and after a set of experiments and the temperature from time to time while the experiments proceeded. The dipping plates were then successively adjusted at definite distances from the sides of the tanks by the introduction of suitable gauges of metal or wood. For each such distance a vibration trace was obtained.

Results.—The chief results of the experiments are given in the photographic reproductions in figures 1–24 (Pl. I.), the details applicable to each trace being shown in the accompanying table. The experiments with oil were really carried out before those with the glycerine, for which it proved convenient to adopt other gauges for the thickness of viscous material in use. Hence the double value for oil at the foot of the table, viz., actual observations and deductions for the same thicknesses as adopted for glycerine.

Of the 24 figures on the plate those constituting any one line are obtained from the same liquid. Those in any one column (except the bottom row figs. 21–24 for oil) are obtained by use of layers of the same thickness of viscous liquid.

The significance of the results in this table becomes apparent when graphs are plotted to exhibit the relations involved. Thus in fig. 1, the abscissæ represent the thickness z of the viscous substance and the ordinates represent the logarithmic decrement, being equal to $\log_e 2$ divided by n , the number of half-periods required to halve the amplitude of the vibration. Thus there is a separate graph for each liquid, its position in the diagram depending on the value of the viscosity concerned. Again, in fig. 2 the ordinates are as before, but the abscissæ now give the values of the viscosities, inserted for the glycerine and water from tables in Archbutt and Deeley's 'Lubrication and Lubricants' (pp. 161–164, 1912, 3rd Edition), and corrected for temperature. In this diagram a separate curve appears for each different thickness of the viscous layers. The logarithmic decrement $\lambda_0 = 0.004$ of the pendulum without any liquids in use is shown on the axis of ordinates in fig. 2. It is the excesses of the other logarithmic decrements over this ($\lambda - \lambda_0$), which really measures the effects of the viscosities of the liquids. But this makes no difference to the determination of the viscosity. It may be seen that the other curves approximately converge to this point.

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TABLE CORRELATING VISCOSITIES AND DAMPINGS.

Liquid.	Densities reduced to 20° C.	Viscosities at 20° C.	Actual Temperatures of use.	Mean Viscosities at temp. of use.	Number <i>n</i> of half periods to halve the amplitude.				Values $\frac{\log 2}{n} = \log \text{dec. } \lambda$.		
					Thickness of Viscous Layer.				Thickness of Viscous Layer.		
					mm.	mm.	mm.	mm.	mm.	mm.	mm.
Λ Glycerine and Water V	gm./c.c.	c.g.s.	°C.	c.g.s.	0.62	0.92	1.62	5.0	0.62	0.92	1.62
	1.2518	6.00	16° 6 to 17° 2	7.9	8.0	11.0	12.0	20.5	0.0866	0.0823	0.0577
	1.2466	4.10	17° 4	5.11	* (1)	(2)	(3)	(4)			0.0338
	1.2430	3.30	16° 2 to 17°	4.5	9.0	11.7	18.7	30.5	0.0769	0.0593	0.0371
	1.24115	2.90	17° 8 to 18° 4	3.48	(5)	(6)	(7)	(8)			0.0227
Λ Oil V	1.23225	1.82	14° 5 to 16° 5	2.73	11.7	17.0	22.0	35.5	0.0593	0.0407	0.0315
					(9)	(10)	(11)	(12)			0.0195
					15.7	23.3	30.0	47.0	0.0433	0.0298	0.0229
					(13)	(14)	(15)	(16)			0.0148
					22.3	24.0	34.5	58.0	0.0311	0.0289	0.0207
					(17)	(18)	(19)	(20)			0.0119
Without any Liquid.			Deduced Values for Oil >						0.028	0.0214	0.0145
											0.00866
											0.00866
					Actual Thicknesses of Viscous Layer of Oil.				Actual Thicknesses of Viscous Layer of Oil.		
					mm.	mm.	mm.	mm.	mm.	mm.	mm.
					0.3	0.7	1.4	5.2	0.3	0.7	1.4
					9.5	27	42.5	80	0.073	0.0256	0.0163
					(21)	(22)	(23)	(24)			0.00866
					log. dec. $\lambda_0 = 0.004$.						

* The Arabic numerals in brackets give the numbers of the photographic reproductions of the traces on the Plate.

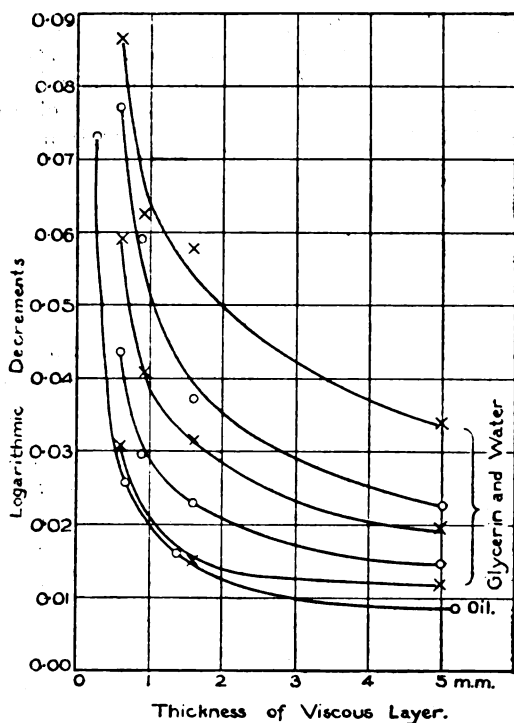
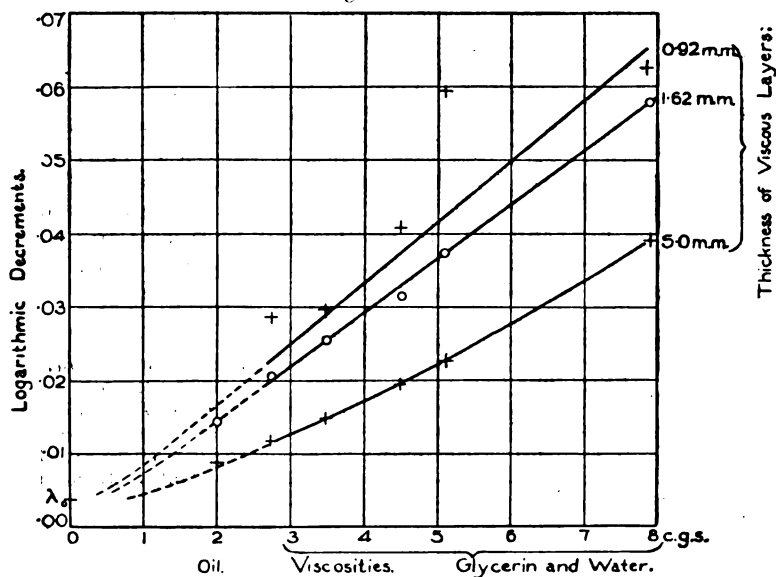


Fig. 1.

Fig. 2.



From the curve plotted for oil on fig. 1, we obtain the ordinates corresponding to the thicknesses used in the experiments on glycerine. And these are inserted in the table and plotted for oil in fig. 2. Thus the viscosity of the oil is determined to be 2 c.g.s. units, by extrapolation from the values for glycerine.

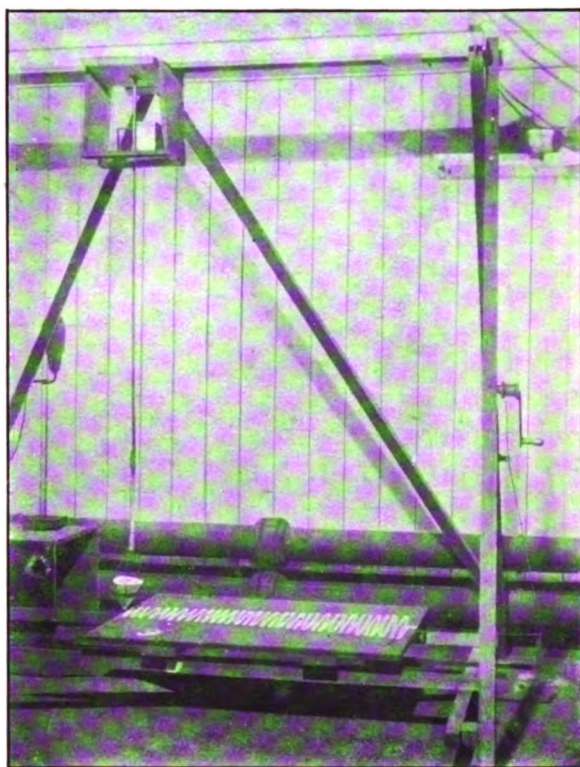
Nottingham,
December 11th, 1923.

XLIII. *Experiments on the Artificial Disintegration of Atoms.*
By Dr. GERHARD KIRSCH, Vienna, and Dr. HANS PETTERSSON, Gothenburg*.

IN the course of a still unfinished series of attempts to accelerate the radioactive disintegration Uranium I—Uranium X through intense bombardment with α -particles, one of us has found a new method for obtaining strong preparations of radium C from radium emanation †. With the simplest type of apparatus used for this purpose, a vertical cylinder of best Invar steel, ground conical at its upper end so as to fit into the neck of a small quartz recipient containing dry radium emanation, has its lower end kept immersed in liquid air. The upper end of the cylinder is covered with a thin foil of the metal to be activized, or else it carries a thin disk of the same material screwed into the steel. The emanation rapidly freezes out on the cooled surface, where it is kept in frozen condition for a couple of hours, so as to leave sufficient time for the active deposit to accumulate. The steel is then heated to room temperature while the emanation is pumped off, the activized metal is purified from emanation by the ordinary method and its γ -activity is measured. The yield of radium C, which is generally between 40 and 50 per cent., may be considerably increased, in fact nearly doubled, by covering the frozen emanation as soon as it has settled on the metal with a piece of very thin metal

* Communicated by the Authors.

† H. Pettersson, *Mit. Inst. f. Radiumforschung*, Nr. 155, *Wiener Ber.* Bd. 132, p. 55 (1923). Owing to other work intervening, the experiments to be described in this paper, which were started in April 1922, have had to be discontinued twice. As they will now again be interrupted for at least several months, we have decided to publish a brief report on the results hitherto gained, although they are mainly methodical in character.



PHOTOGRAPH OF APPARATUS.

leaf, impermeable to the recoil atoms but of sufficiently low stopping-power to the α -particles to be used as "source" together with the activized disk or foil.

By the remarkable experiments made by Sir Ernest Rutherford, partly in collaboration with Dr. J. Chadwick, the artificial disintegration of certain chemical elements has been achieved for the first time*. By the impact with the α -particles of high velocity from radium C and from thorium C, hydrogen nuclei of very long range have been expelled from the atoms of six of the lighter elements, viz., boron, nitrogen, fluorine, sodium, aluminium, and phosphorus. The other lighter elements up to calcium inclusive, as well as certain of the heavier elements, were tested for the same effect but with negative results.

Having at our disposal, thanks to the condensation method, means for obtaining very strong preparations of radium C, we decided to apply this method also for disintegration experiments with some of the lighter elements.

Our first objective was to study the magnetic deflexion of the H-particles from aluminium with a simple magnetic spectrometer constructed for that purpose. A narrow pencil of H-particles emerging through a slit between two blocks of lead is deflected away from the γ -rays by means of a strong magnetic field, the number of scintillations appearing on a zinc sulphide screen being counted by means of a microscope moved across the field by a micrometer screw. In order to obtain a high intensity of the H-radiation the source should have the same shape as the slit, and we therefore tried to modify the condensation method so as to condense the total amount of emanation on a narrow rectangular strip of aluminium foil, 1 by 10 mm. This proved to be a most difficult task, and a considerable number of different condensation vessels have been devised and tested without very satisfactory results. Finally, the first and simplest type of condensation vessel already described was reverted to, the steel stopper was covered with thin aluminium foil, which, when activized and freed from emanation, was folded into a narrow strip and pressed down into the groove of a screw-head made from aluminium. Using this as a source we were able to count the H-particles from aluminium at a distance between source and screen of 5 cm. and to observe their magnetic deflexion in a field of some 8000 gauss.

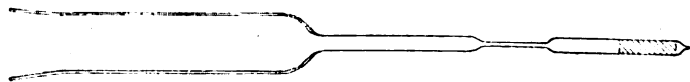
* Rutherford, *Phil. Mag.* xxxvii. p. 581 (1919); Bakerian Lecture, *Proc. Roy. Soc. A*, xcvii. p. 374 (1920); Rutherford and Chadwick, *Phil. Mag.* xlii. p. 809 (1921), *ibid.* xliv. p. 417 (1922).

As the H-particles from aluminium are not homogeneous, the range of the harder particles, according to Rutherford, varying between 30 and 90 cm. of air, the study of their magnetic deflexion practically requires the measuring out of a magnetic spectrum. However, the rapid decay of radium C makes it unsuitable as a source, where prolonged measurements are required, and it therefore appeared most desirable to realize a source of H-particles of more constant activity. A special type of condensation vessel, where frozen emanation itself, condensed on a narrow strip of copper, was to be used as source together with its fellow products under a cover of aluminium leaf, was constructed, but has so far not been put to actual tests, as a much simpler way of realizing the same objective was found in the meantime.

The Capillary Method.

From pieces of "hard" (potassium) glass tubing fine capillaries were drawn out, from 1 to 2 mm. thick and having walls, measured under the microscope, of between 70 and 90 μ . The capillary was sealed up at one end, and over the next 10 mm. of its length the glass was lined inside with a thin sheet of the substance to be examined, equivalent in stopping power to about 2 cm. of air, either as a tiny roll of metal foil pressing well against the glass, or as a fine powder of oxide made to adhere to the glass through heating. An equal length of the glass was left bare for control measurements, and the capillary drawn thin over a short length, subsequently to be drawn out and sealed up after filling it with emanation, fig. 1. The glass tubing with the

Fig. 1.



capillary was then joined to a recipient containing dry emanation mixed with some pure oxygen, which was introduced into the capillary after the latter had been sharply evacuated at a temperature of between 200° and 300° C., so as to remove moisture and absorbed gases. The metal in the capillary had previously been bombarded with cathode rays in a high vacuum in order to remove occluded gases. After sealing up the emanation within the capillary at nearly atmospheric pressure the latter was left for some hours and

its γ -activity measured, the equilibrium amount of radium C varying with different capillaries from 10 to 50 milligrammes.

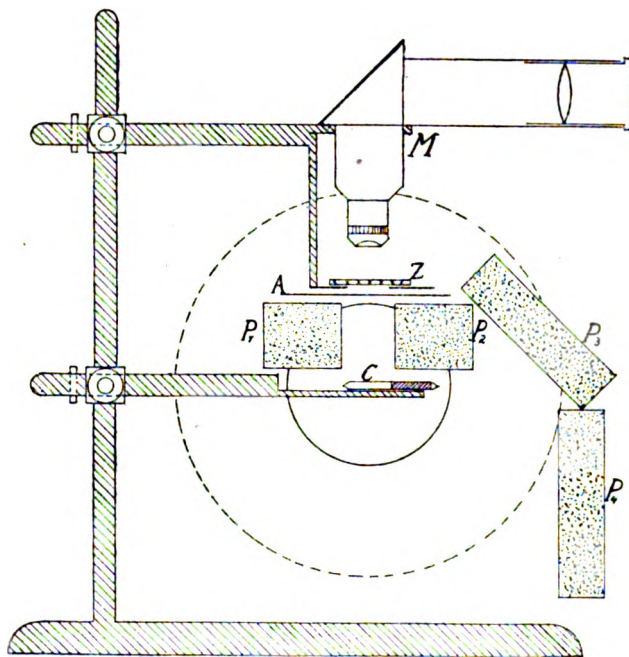
The capillaries made in this manner are very convenient sources of H-particles from, say aluminium. They are easy to manipulate, have the practically linear shape suitable for deflexion experiments, and their use involves no risk of radioactive contamination, as the emanation they contain is hermetically enclosed. Their small dimensions and the way in which they are filled should be a safeguard against contaminations with hydrogen, free as well as in compounds, *i. e.* against the "natural" H-particles which form the most serious source of error in these experiments. Their chief advantage, however, is their constant activity, which declines with the half period of emanation itself, *i. e.* with 3.8 days instead of 20 minutes as with radium C, so that even prolonged measurements may be carried out without change of the source. On the other hand, it must be observed that the α -radiation within the capillary is not homogeneous, as α -particles of three different velocities are being discharged. Also there is some uncertainty about the distribution inside of the most effective component, *i. e.* of radium C. The latter distribution may, however, be changed at will by immersing one end of the capillary in liquid air until the total amount of radium C has accumulated in it.

Method of Observation.

The facilities offered by the method of the capillaries for studying the emission of H-particles from various substances appeared so considerable, that the study of the magnetic spectrum of the H-particles from aluminium was reserved for a future investigation. Instead, a number of capillaries were charged with some of the elements not investigated by Rutherford and Chadwick and were then examined for H-particles. The experimental arrangement is set out in fig. 2. C is the capillary, the unlined part of which is being examined, held by a carrier between the poles of a Leyboldt electromagnet. P_1 and P_2 are blocks of lead (in certain experiments of tungsten) jammed between the poles, which are 6 to 7 mm. apart. The lead serves as a screen against the radiation from the other part of the capillary. Similar blocks of lead P_3 and P_4 protect the eyes of the observer against the γ -radiation from the capillary. The scintillations appearing on the zinc sulphide screen Z are counted through the microscope M, whereas absorbing screens of different stopping power are introduced at A or, in some cases, laid

immediately over the capillary. The microscope closely resembles that described by Rutherford, the objective being a Watson holoscopic of 16 mm. focal length and numerical aperture 0.45, whereas the eyepiece is a wide-field ocular from Zeiss. Without diaphragm the field of view had a diameter of nearly 5 mm., so that the total area observed was practically $1/6$ sq. cm. The light-gathering power of

Fig. 2.



this microscope considerably exceeded that of any other combination tried by us. Nevertheless the scintillations produced by the H-particles are very faint, especially near the end of their range, so that the counting of scintillations, which was generally carried out at night, could not be made for more than one to two minutes at a time by each observer. When the scintillations were very numerous the period was limited to half a minute or even less. Three to

four counters alternated, their results being generally in good accordance with one another.

The quality of the screen is very important in these measurements. Most of the screens used we made ourselves from Sidot blende, but ready-made screens from Harrison Glew were also used with satisfactory results. The background of the screen was constantly illuminated by the γ -radiation from the capillary, which, however, seemed to vary considerably with the nature of the substance enclosing the emanation. With thin copper foil, used instead of the glass in experiments to be described later, the luminosity was much fainter than with glass, thus allowing the distance from source to screen to be considerably reduced.

Results with the Capillary Method.

The H-particles from aluminium are easily observed by the method just described. The number of penetrating H-particles found at different countings agrees well with the value given by Rutherford and Chadwick, *i.e.* about $2.10^{-6} Q$, where Q is the total number of the impinging α -particles from radium C. Consequently with a field of view equal to ours, $1/6$ sq. cm. at a distance of 15 mm. from source to screen, the number of scintillations observed from a capillary containing only one millicurie of emanation behind the aluminium lining should be about 20 per minute, provided the efficiency of the screen is equal to 0.75.

Control countings, when the unlined part of the glass capillary was examined, also gave a definite number of long range particles equal to about one-tenth of those from aluminium. These particles are, no doubt, expelled from sodium atoms in the glass. With capillaries drawn from "Jena Rotstrichglas" the number of these particles was considerably larger, in accordance with the composition of that glass, into which enter not only sodium but also certain amounts of boron and aluminium. Glass is therefore obviously not suitable as material for capillaries to be used for testing other elements for H-particles. For this reason we have instead drawn capillaries from pure fused silica, which is known to be quite free from impurities and which moreover presents the advantage that it can be very energetically heated, so as to drive off moisture and occluded gases from the substance with which it is charged before introducing the emanation.

Quartz capillaries drawn to the shape already described,

some 20 mm. in length, were coated inside over one half of their length with the following substances: scandium oxide, prepared from very pure oxalate of scandium, which had been kindly put at our disposal by Prof. R. I. Meyer of Berlin; vanadium tetroxide, cobalt oxide, and arsenium, the latter element in the shape of a thin mirror, deposited inside the capillary by the Marsh procedure. The last-named capillary could, of course, not be effectively heated, owing to the volatility of the metal.

The scintillations produced by these capillaries on a zinc sulphide screen at different absorptions were counted by means of the arrangement sketched in fig. 2. The results proved, that if any H-particles at all of a range exceeding that of the natural particles are expelled from the atoms of these four elements, the ratio between their number, n , and that of the impinging α -particles, Q , is certainly less than 5 per cent. of the value for aluminium, i. e. $n/Q < 1:10$. A very small number of scintillations, from 1 to 2 per minute, was actually observed with an absorption equal to or exceeding 30 cm. of air with all these substances. Owing to the scarcity of the particles producing these scintillations, their maximum range could not be determined, and it must be left for future investigations to explain their origin.

The number of scintillations appearing at lower values of the absorption down to about 11 cm. of air was, with two exceptions, practically the same, proving that hydrogen contaminations producing natural H-particles were practically absent from the capillaries. One of these exceptions was the arsenium capillary, from which nearly 10 scintillations per minute were counted with an absorption of about 12 cm. air*, whereas at 30 cm. the number was only a little more than 1 per minute. Further experiments will have to be made with this element, but we are inclined to regard these scintillations as due to natural H-particles from hydrogen occluded by the metal.

The other exception was observed with the unlined part of the scandium capillary, which happened to be the most thin-walled of all, so that it could be examined with a total absorption of only 11 cm. A relatively large number of

* Owing to the irregular shape of this capillary there is considerable uncertainty with regard to this value. In view of later results, it does not appear impossible that these H-particles were expelled from the silicon atoms in the capillary walls.

scintillations of unmistakable H-particle type was then observed, viz. over 22 per minute, corresponding to a value of about $5:10^7$ for the quotient n/Q . This number was reduced to less than one-seventh, viz. 3 scintillations per minute, when the absorption was increased to 16 cm. of air by the introduction of a mica filter of 5 cm. air equivalent. This fact alone practically excludes the possibility that these scintillations could have been caused by natural H-particles from any hydrogen contamination within the capillary, which, moreover, would inevitably have given rise to similar particles also from the other part of the same capillary with its thin lining of scandium oxide, equal to about 2 cm. of air.

The only possible way of explaining these scintillations appears to be, that they are caused by H-nuclei expelled from the silicon atoms in the quartz. The other element present, viz. oxygen, has been examined by Rutherford for similar particles with negative results down to an absorption of 9 cm. of air, whereas with silicon the same test has only been carried down to the limit of 17 cm. We therefore infer from this result, which has since been confirmed with other quartz capillaries of still thinner walls, that the silicon atoms under intense bombardment with α -particles break down in a manner similar to that of the elements disintegrated in the experiments of Rutherford and Chadwick, emitting H-particles of the maximum range between 11 and 16 cm. of air. Owing to the difficulty of determining exactly the thickness and the air equivalent of the quartz walls of the capillaries used in these experiments, the numerical values just given are uncertain to a few cms. of air. Experiments made by a somewhat different method and with elementary silicon instead of quartz, have made it possible to fix the maximal range of the H-particles from silicon more nearly at about 12 cm. of air.

Experiments with a Copper Foil Apparatus.

The unexpected results found with silicon forced us to give up quartz capillaries as suitable containers for disintegration experiments, where substances are to be tested for H-particles of short range. On the other hand, it appeared important to pursue that particular kind of investigation with some of the lighter elements found "non-active" in the experiments of Rutherford and Chadwick. We have therefore constructed a different kind of disintegration vessel,

where the thin silica wall of the capillaries is exchanged for a very thin membrane of pure copper*.

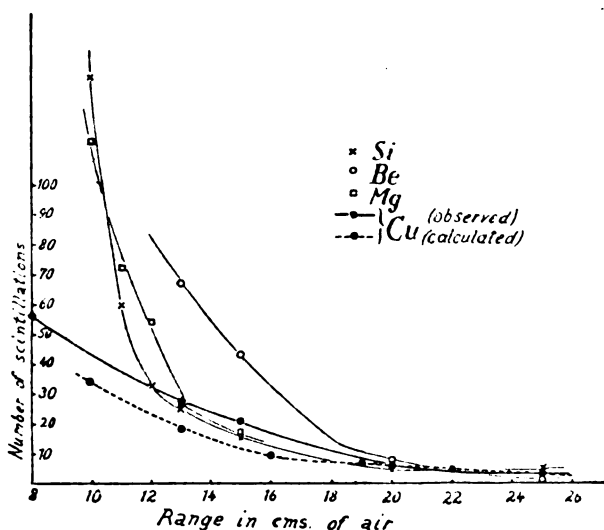
In a brass piece, 2 mm. thick and 6 mm. broad, a slit 2 mm. wide and 45 mm. long is cut out. A strip of unperforated copper foil, about 11μ thick, is soldered over one opening of the slit thus forming a narrow trough, 2 by 2 by 45 mm. long, which can be hermetically closed by soldering a brass lid over its other opening. Four cross-pieces of brass are also soldered across the trough, dividing it into four compartments, which communicate with another by narrow slits immediately under the lid. Before soldering on the lid the substances to be studied are spread as uniformly as possible over the copper foil, one in each compartment, leaving only one compartment empty for control measurements. The area covered by each substance is thus 2 by 10 mm., and the average thickness of the layer is made equivalent in absorbing power to about 2 cm. of air. To charge this apparatus with emanation in the ordinary way by first evacuating it would expose the thin copper and the soldering to dangerous stress. It is therefore filled with emanation at ordinary pressure by means of the following contrivance. At one end the trough communicates with a minute brass mortar, in which a small glass capillary, sealed up with some 40 to 50 millicuries of dry radium emanation mixed with dry and pure oxygen, is crushed beneath a mercury seal by pushing home a small steel rod. At the other end the trough communicates through a fine tin tube with the atmosphere, so as to allow the excess air to escape when the capillary is being crushed. Immediately afterwards the tin tube is soldered off, enclosing the emanation from the crushed capillary hermetically within the trough, about 10 millicuries being enclosed within each compartment. The particles emerging downwards through the copper foil are counted from each division separately by an arrangement similar to that in fig. 2, save that the microscope with the zinc sulphide screen has to be mounted beneath the poles of the electromagnet and in inverted position, the objective directed upwards. As the air equivalent of the copper foil is less than the range of the α -particles from radium C, the latter are absorbed by filters of thin silver foil. These have previously been deprived of occluded gases, as has also the copper foil used in the

* A more complete description of this apparatus is published in the *Sitzungsberichte der Wiener Akademie der Wissenschaften* IIa, July 12th, 1923.

apparatus, by prolonged bombardment with cathode rays in a high vacuum. In order to remove all traces of hydrogen compounds the substances exposed within the trough have been heated and the trough itself, after being charged with the substances but before the emanation is introduced, has been washed out with a current of dry and warm oxygen.

The thin-drawn curves in fig. 3 represent the number of scintillations counted at different absorption values (produced by filters of thin mica) when the trough was charged with the following substances: beryllium oxide, magnesium oxide, and elementary silicon. The number of scintillations

Fig. 3.



from the empty division, *i. e.* from the bare copper foil, is given by the full-drawn, thicker curve. At absorption values exceeding 20 cm. of air the latter curve is seen to coincide practically with the three first-named curves, whereas for absorption values less than 18 cm. the beryllium curve rises rapidly, and the same applies to the curves for magnesium and silicon at the absorption values 13 cm. and 12 cm. respectively. The conclusion appears to us unavoidable, that this considerable excess in number of short-range particles from the considered three elements over the similar particles from copper alone, must be due to H-particles expelled from

the atoms of Be, Mg, and Si by the α -particles discharged within the trough. Without regard to the absorption within the substances we may therefore say, that the three elements investigated have been found to give off H-particles of the approximate maximal ranges: Be, 18 cm.; Mg, 13 cm.; and Si, 12 cm.

Regarding the particles from the bare copper foil the shape of their absorption curve does not seem to exclude the assumption that they may be due to traces of hydrogen contamination occluded in the metal and not completely driven off by the cathode rays. Thanks to the careful measurements made by Sir Ernest Rutherford on the absorption of natural H-particles expelled by α -particles of different velocities *, it is possible to compute a theoretical absorption curve for H-particles derived from such occluded hydrogen, under the assumption that this contamination is evenly distributed within the copper and with due regard to the fact that α -particles of three different initial velocities are active. The broken curve in fig. 3 represents a theoretical absorption curve for natural H-particles calculated in this manner, and drawn to such a scale that it coincides with the experimental curve for copper for absorption values exceeding 20 cm. of air. Also at lower absorption values the differences between the two latter curves are seen to be relatively small, considering that the theoretical curve cannot be very exactly defined. If, on the other hand, the hydrogen contamination were assumed to be differently localized within the copper, or to occur only over its inner surface, the theoretical curves, which can then be calculated, are very similar to the broken curve in the diagram. Whether there are any H-particles of a range exceeding 8 cm. of air expelled from copper atoms or not, must at present be left an open question. Anyhow, it seems hardly possible to attribute the large excess in the H-particles of shorter range expelled from the charged divisions over those from copper alone to any other reason than a disintegration of the atoms in the substances.

It may be added, that a much larger number of scintillations was observed from the three elements investigated, at a minimal value of absorption equal to 8 cm. of air, namely, from beryllium about 400 per minute, and from magnesium and silicon between 250 and 300 per minute. These numbers being too large for direct countings, they were instead estimated independently by the different observers, and an

* Rutherford, *Phil. Mag.* xxxvii. p. 550 (1919).

average value was formed. The corresponding points are not set out in the diagram, partly for want of space, partly, also, owing to the higher degree of uncertainty of these estimated numbers.

In another series of similar measurements the trough was charged with carbonate of lithium, sulphide of copper, and chloride of silver, one division being as usual left bare for control. The number of scintillations from this division was, however, at these experiments considerably larger than before, probably owing to a stronger contamination by occluded hydrogen, so that no definite results could be inferred with regard to sulphur and chlorine. For lithium the results appeared to establish as fairly certain the emission of H-particles of the maximum range equal to some 10 cm. of air.

In the following table the results hitherto obtained with regard to atomic disintegration by α -particles are set out, according to our own experiments as well as to those of Rutherford and Chadwick. The ranges of the expelled H-particles given in the second column refer to particles in the forward direction. Whether the elements disintegrated by us emit particles also in the backward direction has not yet been investigated.

Judging by analogy with Rutherford's results, the range of such backward particles should be considerably less than that of those directed forwards and correspondingly more difficult to investigate.

TABLE I.

Element.	Atomic number.	Atomic mass.	Range of H-particles.
Lithium	3	6 : 7	10 cm.
Beryllium	4	9	18 cm.
Boron	5	10 : 11	58 cm.*
Nitrogen.....	7	14	40 cm.*
Fluorine.....	9	19	65 cm.*
Sodium	11	23	58 cm.*
Magnesium	12	24 : 25 : 26	13 cm.
Aluminium	13	27	90 cm.*
Silicon	14	28 : 29	12 cm.
Phosphorus	15	31	65 cm.*

* According to Rutherford and Chadwick, Phil. Mag. xlv. p. 425.

Future Investigations.

The methods described in this paper offer facilities for further research on atomic disintegration. With an apparatus similar to the one last described, the different elements of the periodic system may be investigated for H-particles of a range barely exceeding that of the α -particles from radium C, possibly, with the aid of a strong magnetic field, also for particles of still shorter range.

Preparations are being made in this Institute to utilize the method of capillaries for making the H-rays from aluminium and from other disintegrable elements visible by the Wilson method. It is to be hoped that one may in this way also be able to decide, whether one or more H-particles are expelled from the same disintegrating atom.

We wish, in conclusion, to express our sincerest gratitude to Professor Stefan Meyer for generously putting the resources of the Radium Institute at our disposal, as well as for the kind interest he has taken in our research.

Summary.

A new method for obtaining strong preparations of radium C from radium emanation by condensation with liquid air is described.

Two different methods have been worked out for studying the particles expelled from artificially disintegrated atoms.

The elements Sc, Va, Co, and As have been investigated for H-particles of a range exceeding about 17 cm. of air, the results proving that such particles, if expelled at all, are certainly less numerous than one-twentieth of the particles expelled from aluminium.

As a first result of the same methods applied to the study of short-range particles, the following three elements have been found to give off H-particles under bombardment with α -particles, namely: beryllium, magnesium, and silicon, whereas for lithium the evidence of disintegration is less conclusive.

Some lines for further research are indicated.

Institut für Radiumforschung,
Wien, July 1923.

XLIII. The Molecular Association of Liquids and Highly-Compressed Gases.—Part III. The Molecular Association of Liquids. By E. E. WALKER, D.Sc., D.I.C., A.C.G.I.*

ACCORDING to the law of corresponding states the critical coefficient $\left(\frac{d\pi}{d\theta}\right)_c$ should be the same for all substances. Van der Waals has shown that, though this is not strictly the case, it† is a function of the ratios $\frac{RT_c}{P_c V_c}$. In Part I.‡ it was shown that this ratio is a function of the length of the molecule, and it follows from this that $\left(\frac{d\pi}{d\theta}\right)_c$ is also a function of this quantity. Many authors have pointed out that this coefficient and the related coefficient “*f*,” which is defined by the equation

$$f = \frac{\log \frac{1}{\pi}}{\frac{1}{\theta} - 1},$$

are dependent on the size of the molecule, and that only substances of approximately the same molecular size obey the law of corresponding states, but its correlation with the length of the molecule makes it possible to give the conception quantitative form. In fact, one may restate the law of corresponding states as follows:—

The relationships existing between the true reduced temperatures, pressures, and volumes of all substances, the molecules of which have the same length, are very nearly identical.

Before proceeding to examine the validity of this statement, it is necessary to explain what is meant by the terms “true reduced temperatures, pressures, and volumes.” The reduced coordinates of an unassociated substance are respectively $\frac{T}{T_c}$, $\frac{P}{P_c}$, and $\frac{V}{V_c}$. In the case of associated substances these simple ratios give only the apparent reduced coordinates. To obtain the true reduced quantities it is

* Communicated by the Author.

† This refers to the values obtained from the vapour-pressure curve. The values deduced from the critical isometries are slightly different.

‡ Phil. Mag Jan. 1924, p. 111.

necessary to substitute for T_c , P_c , and V_c those critical constants which would have been observed if the liquid could have been raised from the temperature T to the critical point without any change in the equilibrium between the simple and associated molecules. In Part II.* a method of estimating the effect of varying degrees of association on the critical constants was devised, and the equations deduced in that paper may be used to calculate the true reduced coordinates of an associated substance.

Let θ_a , π_a , V_a be the apparent reduced coordinates,
 θ_t , π_t , V_t be the true reduced coordinates,
 n be the association factor at a given temperature,
 and n_c be the association factor at the critical point,
 then by equations (6), (7), and (8) of Part II. :—

$$\theta_t = \theta_a \times \left(\frac{n}{n_c}\right)^{-\frac{1}{3}-x+\frac{2}{3}y}, \quad \dots \quad (1)$$

$$\pi_t = \pi_a \times \left(\frac{n}{n_c}\right)^{+\frac{2}{3}+x+\frac{6}{3}y}, \quad \dots \quad (2)$$

$$V_t = V_a \times \left(\frac{n}{n_c}\right)^{-x-y}. \quad \dots \quad (3)$$

x and y have been defined in Parts I. and II. They may be calculated from the length of the molecule as follows :—

$$x = 3.33 \log_{10} \frac{.838 + .174 \log_{10} 2l}{.838 + .174 \log_{10} l},$$

$$y = 3.33 \log_{10} \frac{1 + \frac{12.2}{8l^3}}{1 + \frac{12.2}{l^3}}.$$

If the modified law of corresponding states holds good for liquids containing simple and associated molecules in equilibrium, then it should be possible to determine $\frac{n}{n_c}$ for any given liquid by equating its true reduced coordinates with those of a saturated normal paraffin having a molecular length equal to the average molecular length ($n \times l$) of the associated substance. For the present it will be assumed that the modified law holds good both for associated and

* Phil. Mag. Jan. 1924, p. 117.

unassociated liquids, and the validity of this hypothesis must be judged after an examination of the results achieved by its application to the problem of molecular association.

In order to obtain values of $\frac{n}{n_c}$ for an associated liquid, any two of the three coordinates may be chosen and equated with the corresponding coordinates of a normal paraffin having the same molecular length. The necessary data for the lower paraffins are, however, scanty, and those for the vapour-pressure curves are most easily interpolated. It is on this account that the first calculations have been made from temperatures and vapour pressures.

The reduced temperature of any liquid normal paraffin may be calculated with sufficient accuracy from the expression :

$$\theta = \frac{\theta_p}{1 - C(1 - \theta_p)}.$$

Where θ is the reduced temperature of the liquid and θ_p is the reduced temperature of normal pentane under the same reduced pressure. The values of C found for various normal paraffins are given in Table I.

TABLE I.

	C.	<i>l.</i>	C.
Methane	-.222*	3	-.220
Ethane	-.152	4	-.175
Propane	-.0943	5	-.135
Butane	-.045	6	-.099
Pentane	±.0000	7	-.066
Hexane	+.0398	8	-.035
Heptane	+.0772	9	-.006
Octane	+.1062	10	+.021
		11	+.046
		12	+.070
		13	+.097
		14	+.109

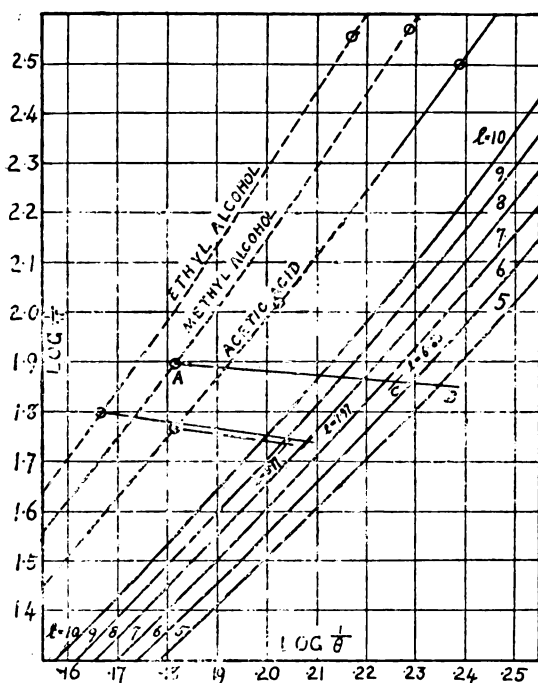
* By extrapolation.

Values of C corresponding with various integral molecular lengths have been determined from these data by graphical interpolation, and are recorded in the same table. From these values and Young's data for pentane, curves can be constructed connecting true reduced temperatures (θ_i) with true reduced pressures (π_i) for any length of molecule. In

the case of an associated substance the problem is to find what value of $\frac{n}{n_c}$ will satisfy equations (1) and (2). This can be solved by the following graphical construction.

Values of $\log \frac{1}{\pi_t}$ are plotted as ordinates against values of $\log \frac{1}{\theta_t}$ as abscissæ for various lengths of molecule. A similar $\log \frac{1}{\pi_a}, \log \frac{1}{\theta_a}$ curve is plotted for the associated substance.

Fig. 1.



Portions of these curves are shown in fig. 1, the dotted curves being for methyl alcohol, ethyl alcohol, and acetic acid. Through any required point A on the desired curve a straight line AB is drawn with a slope of

$$\frac{-\frac{1}{3} - x + \frac{2}{3}y}{+\frac{2}{3} + x + \frac{5}{3}y}.$$

The point C representing the logarithms of the true reduced

coordinates of the associated substance must be on this line, and it must be also on the $\log \frac{1}{\pi_t}, \log \frac{1}{\theta_t}$ curve for a substance of molecular length equal to $n \times l$. This point can be fixed by means of a few trials without any difficulty. Fig. 1 represents part of the diagram used in determining the association factors of ethyl alcohol and acetic acid at various temperatures.

Values of $\frac{n}{n_c}$ for the saturated, normal paraffins are necessarily unity by this method, since they are chosen as the standards against which all other substances are compared.

Values of $\frac{n}{n_c}$ for other hydrocarbons at the atmospheric boiling-point are recorded in Table II. According to these,

TABLE II.

	l	$-\frac{1}{3}-x+\frac{1}{2}y$	$+\frac{2}{3}+x+\frac{1}{2}y$	n_c	$\frac{n_b}{n_c}$	n_b
Normal paraffins.	...	...	...	1·00	1·00	1·00
Iso-pentane 7·56	—·431	+·683	1·005	1·017	1·02	
Di-iso-propyl 7·56	·431	·683	1·007	1·030	1·035	
Di-iso-butyl 10·74	·415	·718	1·00	1·024	1·025	
Hexamethylene... 7·30	·432	·675	1·00	1·019	1·02	
Benzene 7·30	·432	·675	1·012	1·017	1·03	
Acetylene 4·58	·511	·492	...	1·061	...	
Ethylene 4·58	·511	·492	...	·996	...	

“iso”-structure induces traces of association. It cannot be stated for certain that these traces of association are genuine, they might be due to inaccuracies in the modified law of corresponding states. If this is so, the errors are not large. It may be mentioned, however, that the addition of methyl groups as a rule enhances molecular association, and therefore these traces of association may well be genuine. Acetylene is quite appreciably associated but ethylene is not, the critical volumes of these substances are not known, so that n_c cannot be calculated with accuracy, but an examination of the other critical constants indicates that acetylene is more highly associated than ethylene at the critical point. In this and succeeding tables it should be noted that the value of $\frac{n_b}{n_c}$ is never appreciably * less than unity, thus

* Ethylene is the only case which has been observed, but this may be regarded as unity within experimental error.

justifying the selection of the normal paraffins as comparison substances. Whether they are associated or not, they appear to be the least associated of all substances.

Similar data for a variety of slightly associated organic compounds are recorded in Table III. It will be observed

TABLE III.

	<i>l.</i>	$-\frac{1}{3}-x+\frac{2}{3}y.$	$+\frac{2}{3}+x+\frac{5}{3}y.$	$n_c.$	$\frac{n_b}{n_c}.$	$n_b.$
Methyl formate.....	6.43	-.447	+.649	1.062	1.053	1.12
Ethyl formate	7.97	.427	.691	1.041	1.037	1.08
Propyl formate.....	9.51	.418	.710	1.022	1.032	1.055
Methyl acetate	7.42	.433	.680	1.057	1.065	1.125
Ethyl acetate.....	8.96	.421	.703	1.046	1.055	1.105
Propyl acetate	10.50	.415	.718	1.031	1.043	1.075
Methyl propionate..	8.96	.421	.703	1.035	1.051	1.09
Ethyl propionate ...	10.50	.415	.718	1.028	1.039	1.07
Methyl butyrate ...	10.50	.415	.718	1.023	1.037	1.06
Methyl-iso-butyrate	8.96	.421	.703	1.025	1.052	1.08
Ethyl ether	8.96	.421	.703	1.012	1.019	1.03
Methyl chloride	4.39	.523	.461	1.065	1.042	1.11
Carbon tetrachloride	5.74	.461	.611	1.010	1.024	1.035
Stannic chloride ...	7.00	.438	.669	1.011	1.032	1.045
Fluorbenzene.....	7.90	.427	.691	1.017	1.022	1.04

that the degree of association at the boiling-point is, as a rule, approximately twice that at the critical point. Among isomeric esters the acetates are more highly associated than either the formates, propionates, or butyrates. The methyl group appears to exert a specific influence in this and other cases. Thus, for example, methyl chloride is more highly associated than carbon tetrachloride.

TABLE IV.

	<i>l.</i>	$-\frac{1}{3}-x+\frac{2}{3}y.$	$+\frac{2}{3}+x+\frac{5}{3}y.$	$n_c.$	$\frac{n_b}{n_c}.$	$n_b.$
Methyl alcohol	4.34	-.527	+.451	1.259	1.214	1.53
Ethyl alcohol	5.88	-.459	+.620	1.097	1.233	1.355
Propyl alcohol	7.42	-.433	+.650	1.072	1.189	1.275
Acetic acid.....	5.88	-.459	+.620	1.341	1.118	1.49
Acetonitrile	5.13	-.483	+.562	1.470	1.077	1.585
Propionitrile	6.67	-.442	+.657	1.305	1.030	1.345
Water.....	2.80	-.782	-.174	1.270	1.12	1.42
Ammonia	2.80	-.782	-.174	1.091	1.11	1.21
Hydrogen chloride.	2.85	-.768	-.141	1.057	1.40	1.48

Data for more highly associated substances are recorded in Table IV. Among these substances there is no clear

relationship between the degree of association at the boiling-point and that at the critical point, though the nitriles are peculiar in that, although they are highly associated at the critical point, they are only very slightly more associated at the boiling-point. This fact appears to account for certain peculiarities of these substances. Some methods indicate that they are normal substances, and others that they are associated*. Thus the Trouton constant for the nitriles is practically normal and their rectilinear diameter is remarkably straight. The table shows that this method of measuring molecular association is in agreement with the Rose Innes surface-tension method in indicating that methyl alcohol is more associated than water. Walden's molecular cohesion method gives the same result, and it seems that in this case also the methyl group is exerting a specific influence.

The method is applicable to all temperatures, and the association factors have been worked out over a wide range of temperatures for the alcohols and acetic acid. The values

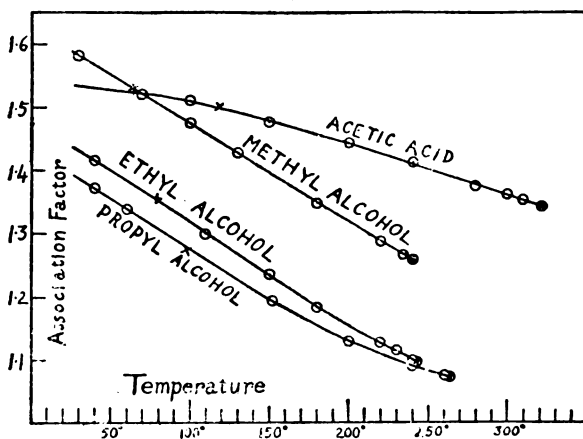
TABLE V.

Methyl alcohol.			Ethyl alcohol.		
<i>t.</i>	$\frac{n}{n_c}$	<i>n.</i>	<i>t.</i>	$\frac{n}{n_c}$	<i>n.</i>
30	1.258	1.584	40	1.291	1.416
64.7 B.P.	1.214	1.528	78.3 B.P.	1.235	1.354
100	1.171	1.474	110	1.184	1.299
130	1.135	1.429	150	1.126	1.235
180	1.070	1.347	180	1.079	1.182
220	1.023	1.288	220	1.028	1.128
234	1.007	1.268	230	1.017	1.116
238	1.002	1.262	240	1.002	1.099
240.0 C.	1.000	1.259	243.1 C.	1.000	1.097
Propyl alcohol.			Acetic acid.		
40	1.279	1.371	70	1.132	1.518
60	1.249	1.339	100	1.124	1.507
97.4 B.P.	1.189	1.275	118.5 B.P.	1.118	1.491
150	1.115	1.195	150	1.100	1.489
200	1.053	1.129	200	1.076	1.443
240	1.019	1.092	250	1.051	1.409
260	1.004	1.076	280	1.024	1.373
263.7 C.	1.000	1.072	300	1.014	1.360
			310	1.008	1.352
			321.6 C.	1.000	1.341

* See Ter Gazarian, *J. Chim. Phys.* iv. p. 140 (1906).

are recorded in Table V., and are plotted against temperature in fig. 2. It is very surprising that the rapid change in volume which takes place in the neighbourhood of the critical point should not produce a correspondingly marked change in the association factor. It appears that in this highly condensed state the volume has but little influence on the degree of association which is almost solely a function of the temperature.

Fig. 2.



Curves showing variation of association factors with temperature.

× indicates boiling-point.

⊕ indicates critical point.

It has been pointed out that, if the modified law of corresponding states is true generally, it should be possible to determine the association factor from any two reduced

coordinates. Thus, it should be possible to determine $\frac{n}{n_c}$

from the apparent reduced volumes and apparent reduced temperatures. An attempt has been made to do this, using equations 2 and 3 and employing a method somewhat similar to that just described. The results are, however, vitiated by the fact that only scanty data are available for the lower paraffins. These data are less easy to interpolate than the vapour-pressure data, and somewhat doubtful extrapolation has been necessary in some cases. The method will not be described here in detail, as it is hoped that it may be found possible to improve it, but some results which have been obtained are quoted in Table VI., as they give considerable

TABLE VI.

Acetic Acid.				Methyl Alcohol.				Ethyl Alcohol.			
Apparent reduced volume.	Temperature.	Volume method. n	Vapour-pressure method. n	Temperature.	Volume method. n	Vapour-pressure method. n	Temperature.	Volume method. n	Vapour-pressure method. n	Temperature.	Volume method. n
.38	130.7	1.47	1.49	98.0	1.53	1.48	89.9	1.34	1.34		
.40	164.8	1.46	1.47	127.3	1.52	1.43	122.8	1.33	1.28		
.45	228.6	1.42	1.42	176.3	1.44	1.35	172.5	1.24	1.20		
.55	288.8	1.37	1.37	218.8	1.32	1.29	218.3	1.14	1.12		
.75	...	...	...	238.5	1.27	1.26	242.2	1.11	1.10		
1.00	321.6	1.34	1.34	240.0	1.26	1.26	243.1	1.10	1.10		

support to the hypothesis which forms the basis of this communication. The association factors calculated by the two methods are on the whole in good agreement, and, though the values calculated from reduced volumes must be regarded as provisional, they afford valuable evidence in support of the main contentions put forward in this paper. So far as the author is aware, there is no reason why this measure of agreement should be obtained unless

- (a) The modified law of corresponding states holds good for these associated substances.
- (b) The method of calculating the true reduced coordinates is true as a first approximation.

No such measure of agreement would be obtained if the hypothesis were altered in any important particular. Thus, for instance, in calculating the true reduced coordinates, it was assumed (see Part II., *loc. cit.*) that the molecules are joined end to end, so that the length of a double molecule is twice that of a single one. If the assumption is made that the molecules are joined side by side, so that the length of a double molecule is the same as that of a single one, the calculation of the true reduced coordinates becomes very much simplified, since x and y in equations (1), (2), and (3) become equal to zero. The association factors calculated on this hypothesis are considerably higher, and the agreement between the two methods is distinctly less satisfactory.

TABLE VII.

	Methyl alcohol. n	Ethyl alcohol. n	Acetic acid. n	
Vapour-pressure method.	1.81	1.53	1.78	Molecules side by side, x & $y=0$, Mean divergence=11.6 per cent.
Volume method	2.22	1.43	1.67	
Vapour-pressure method.	1.48	1.34	1.49	Molecules end to end, x & y corrections used. Mean divergence=1.6 per cent.
Volume method	1.53	1.34	1.47	

The association factors of methyl alcohol, ethyl alcohol, and acetic acid at an apparent reduced volume of 0.38 have been calculated on this alternative hypothesis, and are recorded in Table VII. The mean divergence between the results given by the volume and vapour-pressure methods is raised

from 1.6 per cent. to 11.6 per cent. This increased divergence is striking in the case of methyl alcohol, but is less marked in the other two cases. It appears, therefore, that the adoption of the more probable hypothesis is justified in spite of the greater complexity which it introduces into the calculations.

It now remains to consider how far the results obtained have justified the modification of the law of corresponding states proposed in this paper. Firstly, the association factors calculated on the basis of this hypothesis are rational and free from obvious anomalies. Secondly, two different methods of determining the association factor, depending on different physical properties, give values which are in good agreement with one another. A third argument in its favour is the difficulty of finding any reasonable alternative hypothesis. If, for instance, it is assumed that isomers are corresponding substances, then such substances as isopentane, di-iso-propyl, and di-iso-butyl would appear to be actually dissociate $\frac{1}{2}$, their association factors at the boiling-point being several per cent. less than unity, and becoming smaller as the temperature falls. Moreover, we should be left without a guide in the case of substances not isomeric with the normal paraffins. Similar anomalies are observed if it is assumed that substances of equal molecular weight or equal molecular volume obey the law of corresponding states. Sometimes it is stated that substances having equal or nearly equal critical temperatures are corresponding substances, but further anomalies are met with in this case. Iso-pentane, di-iso-propyl, di-iso-butyl, hexamethylene, benzene, carbon tetrachloride, and various other substances would appear to be dissociated, and mercury (which cannot be dissociated) would prove a glaring exception, for its reduced vapour-pressure curve corresponds with those of the monatomic gases, a fact which is in harmony with the hypothesis put forward in this paper, but is entirely contrary to what would be expected if critical temperature or molecular weight were the controlling factor. The association factors calculated in this paper are entirely free from such anomalies, and, though n_t is sometimes only one per cent. greater than n_c , no case has been observed in which it is appreciably less. It cannot be doubted that other dimensions of the molecule besides the length exert some influence on the true reduced coordinates, and that only those substances having exactly the same molecular dimensions are likely to correspond exactly, but the influence of the length appears to be paramount and that of the other dimensions must be small. It is believed,

therefore, that the modified law of corresponding states is a reasonably close approximation to the truth, and that the association factors which have been calculated by means of this hypothesis are at least more reliable than any which have been determined up to the present.

One alternative suggestion as to the exact physical meaning of "*l*" may be put forward here, though it cannot be tested satisfactorily from existing data. It seems probable that "*l*" may represent not merely the length of the molecule but the mean collision area. In the case of normal carbon chains the mean collision area would be very nearly proportional to the length. Side chain formation and ring formation would reduce the mean collision area, though not quite in the same ratio as the reduction in the molecular length. It is possible that the conventionally determined molecular length used in these papers is really a rough estimate of the mean collision area. This could be tested by extensive viscosity measurements on substances belonging to isomeric and homologous series.

The thirty pure instances investigated by Young and his collaborators form the backbone of the experimental data quoted in these three papers. Outside these authors' work there are probably very few critical volumes of organic compounds that can be relied upon. The critical volumes of methane*, methyl chloride, and the nitriles, determined respectively by Cardoso, Baume, and Ter Gazarian, are probably accurate, and all these values have been employed. The only really doubtful critical data which have been used are those for propane† and ammonia. It is hoped that some laboratory equipped for low-temperature research will undertake a thorough study of the lower paraffins comparable with that carried out by Young on pentane, hexane, heptane, octane, and some of their isomers. Such work would fill in an important gap in our knowledge and provide data for

* At the time this paper was written the author was not acquainted with the recent work of Keyes on methane (Journal of Maths. and Physics, Massachusetts Inst. of Technology, August 1922). This work confirms Cardoso's critical constants on the whole, but points out a slight error in his temperature-scale.

† It is found that the critical pressures determined by the older workers—Olzewsky, Nadejine, Altschul, and others—are from two to six per cent. too high. Olzewsky's value for ethane is 2 per cent. high, therefore in these papers it has been assumed that his value for propane is also 2 per cent. high, and in all calculations in these papers the value 43.1 atmospheres has been used instead of the experimental value 44.0. There can be no doubt that the assumed value is very close to the truth. No other critical pressures determined by these authors have been employed in these papers.

determining with greater accuracy the association factors of such highly associated substances as water and ammonia, which, having small molecules themselves, must necessarily be compared with the lower paraffins.

Summary.

A modified law of corresponding states has been proposed. This law indicates that only substances the molecules of which have the same length (or possibly the same mean collision area) are truly corresponding substances. It is shown that this law is applicable to associated substances if proper correction is made for the effect of molecular association on the critical constants. By means of this modified law of corresponding states the association factors of twenty-four substances at the boiling-point have been determined, and these calculations have been extended over a wide range of temperature in the case of the alcohols and acetic acid.

XLIV. *The Influence of the Earth's Rotation on a Top.*

By JOHN LIGHTON SYNGE, M.A.*

THE rotation of the plane of vibration of a pendulum due to the earth's rotation was deduced by Foucault, not on the basis of classical mechanics, but from the empirical assumption that the normal to the plane of vibration tends to set itself as parallel as possible to the earth's axis ('*Travaux Scientifiques*,' p. 382). The application of the same principle to the case of a top rotating on the earth's surface led him at once to the following conclusions:—"If one considers the rotation of the earth, one finds that the position of a top in motion is not that in which its axis coincides with the vertical, but that it corresponds to a certain oblique line contained in the plane of the meridian and which leans south or north according as the top turns to the right or to the left. It is impossible to give the value of the angle which measures the inclination of the top, seeing that this angle varies with the form, the mass, and the velocity of rotation of the apparatus. All one can say is that it increases with the rapidity of the motion, with the moment of inertia of the system, and with the lowering of its centre of gravity below the point of support." (*Op. cit.* p. 410.) He proceeds

* Communicated by the Author.

to describe the apparatus which he employed to observe this effect, states that he observed it, but leaves a blank in the space destined for a quantitative result.

He predicts further that if a top be spun on a horizontal glass plate it will travel from west to east. This is a direct consequence of his previous prediction, for if the axis of the top is inclined to the vertical, the horizontal plane makes contact with the top around a small circle, and the rolling of this small circle on the plane will produce the effect described. He states that he observed this effect, but again the space destined for a quantitative result is left blank.

The object of the present paper is to show, as a result of rigorous treatment, that the effect of the earth's rotation is the reverse of that predicted by Foucault: that for earth-like rotation the inclination is to the south, for the contrary rotation to the north, and thus the direction of travel for either sense of rotation is not from west to east, but from east to west.

Let G be the centre of gravity of the top, V its vertex, and let $VG = a$; let M be its mass, and A, A, C the principal moments of inertia at G . We regard V as a point fixed relative to the earth's surface. Let O be the projection of V on the earth's axis; OZ the earth's axis in the sense south-north; OX, OY fixed directions forming a right-handed system of rectangular axes. Let NV be the direction of the earth's gravitational field at V , and let α be the angle between VN and OZ . Since the top is small, we may regard the earth's field as parallel to NV of uniform intensity g . Let $OV = \rho$. Let (x, y, z) be the coordinates of G , and (θ, ϕ, ψ) Eulerian angles specifying the orientation of the top relative to $(OXYZ)$.

The kinetic energy is given by

$$T = \frac{1}{2}M(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \frac{1}{2}A(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) + \frac{1}{2}C(\dot{\psi} + \dot{\phi} \cos \theta)^2,$$

and the potential energy is Mgp where p is the projection of VG on VN , or

$$p = a \sin \theta \sin \alpha \cos (\phi - \Omega t) + a \cos \theta \cos \alpha,$$

where Ω is the angular velocity of the earth and $y=0$ is the meridian plane through V when $t=0$. We have

$$x = \rho \cos \Omega t + a \sin \theta \cos \phi,$$

$$y = \rho \sin \Omega t + a \sin \theta \sin \phi,$$

$$z = a \cos \theta,$$

Substitution gives

$$\begin{aligned} L = T - V = & \frac{1}{2} M \rho^2 \Omega^2 + \frac{1}{2} A' (\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) + \frac{1}{2} C (\dot{\psi} + \dot{\phi} \cos \theta)^2 \\ & + M \rho \Omega a [\dot{\theta} \cos \theta \sin (\phi - \Omega t) + \dot{\phi} \sin \theta \cos (\phi - \Omega t)] \\ & - M g a [\sin \theta \sin \alpha \cos (\phi - \Omega t) + \cos \theta \cos \alpha], \end{aligned}$$

where A' is the moment of inertia about an axis through V perpendicular to the axis of symmetry. The system is holonomic, specified by coordinates θ, ϕ, ψ , of which ψ is ignorable: thus we have the integral

$$\frac{\partial L}{\partial \dot{\psi}} = C(\dot{\psi} + \dot{\phi} \cos \theta) = \beta, \text{ a constant.}$$

The modified kinetic potential, omitting constants, is

$$\begin{aligned} R = & \frac{1}{2} A' (\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) + \dot{\phi} \beta \cos \theta \\ & + M \rho \Omega a [\dot{\theta} \cos \theta \sin (\phi - \Omega t) + \dot{\phi} \sin \theta \cos (\phi - \Omega t)] \\ & - M g a [\sin \theta \sin \alpha \cos (\phi - \Omega t) + \cos \theta \cos \alpha]. \end{aligned}$$

The equations of motion,

$$\frac{d}{dt} \left(\frac{\partial R}{\partial \dot{\theta}} \right) - \frac{\partial R}{\partial \theta} = 0, \quad \frac{d}{dt} \left(\frac{\partial R}{\partial \dot{\phi}} \right) - \frac{\partial R}{\partial \phi} = 0,$$

become

$$\begin{aligned} A' (\ddot{\theta} - \dot{\phi}^2 \sin \theta \cos \theta) + \beta \dot{\phi} \sin \theta - M \rho \Omega^2 a \cos \theta \cos (\phi - \Omega t) \\ + M g a [\cos \theta \sin \alpha \cos (\phi - \Omega t) - \sin \theta \cos \alpha] = 0, \\ A' (\ddot{\phi} \sin^2 \theta + 2 \dot{\theta} \dot{\phi} \sin \theta \cos \theta) - \beta \dot{\theta} \sin \theta \\ + M \rho \Omega^2 a \sin \theta \sin (\phi - \Omega t) \\ - M g a \sin \theta \sin \alpha \sin (\phi - \Omega t) = 0. \end{aligned}$$

The steady motion will be given by these equations on putting $\theta = \text{constant}$, $\phi = \Omega t$: we find

$$\begin{aligned} -A' \Omega^2 \sin \theta \cos \theta + \beta \Omega \sin \theta - M \rho \Omega^2 a \cos \theta \\ + M g a \sin (\alpha - \theta) = 0 \end{aligned}$$

from the first equation, while the second equation is satisfied identically.

So far we have used no approximation, but now, remembering that Ω is small (while ρ is large), we may omit the first term, and substituting $C\omega$ for β , where ω is the angular velocity of the top about its axis, we obtain

$$M g a \sin (\theta - \alpha) = C \omega \sin \theta - M \rho \Omega^2 a \cos \theta. \quad (1)$$

equilibrium under the influence of three forces : Mg parallel to NV ; the reaction at V having components P along VA and Q along VG , AVG being a right angle ; and the reversed effective force $M\Omega^2\rho$ parallel to OV , where ρ has been substituted for the distance of G from the earth's axis, the ratio VG/ρ being very small. Using the notation of the preceding method, and resolving parallel to VA , we find

$$P + Mg \sin(\alpha - \theta) = M\Omega^2\rho \cos \theta \quad . \quad . \quad (2)$$

Considering now motion relative to the centre of gravity, let $G\xi\eta\zeta$ be axes with directions fixed in space, $G\xi$ being instantaneously coincident with the normal to the plane of the meridian, drawn out from the page, $G\eta$ in the direction VG , and $G\zeta$ parallel to VA . The angular velocity of the top is compounded of the angular velocities Ω about the earth's axis and ω about VG , thus giving as components of angular velocity about $G\xi\eta\zeta$

$$0, \quad \omega + \Omega \cos \theta, \quad \Omega \sin \theta ;$$

and for components of angular momentum

$$0, \quad C(\omega + \Omega \cos \theta), \quad A\Omega \sin \theta.$$

Let GH be the angular momentum vector, and HD perpendicular to GD , a parallel to the earth's axis. Then the components of the velocity of H relative to $G\xi\eta\zeta$ are

$$-\Omega \cdot DH, \quad 0, \quad 0,$$

and these are identical with the moments of forces about these axes, viz. $-Pa, 0, 0$.

Thus

$$-Pa = -\Omega \cdot DH,$$

or since

$$DH = C \sin \theta (\omega + \Omega \cos \theta) - A\Omega \sin \theta \cos \theta,$$

and Ω^2 is small,

$$Pa = C\omega\Omega \sin \theta. \quad . \quad . \quad . \quad (3)$$

Eliminating P between (2) and (3),

$$C\omega\Omega \sin \theta + Mg \sin(\alpha - \theta) = M\Omega^2\rho \cos \theta,$$

which is the relation (1) obtained by the analytical method, and from which the same result follows as before.

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XLV. *Electric Moment and Molecular Structure.* By CHARLES P. SMYTH, *Ph.D., Department of Chemistry, Princeton University* *.

A PREVIOUS paper † has described a method for the calculation of the electric moment of the molecule of a substance from experimental data. The present paper considers the relation between the moments calculated for a number of substances and the structures of the systems of electrons and positive nuclei which constitute the molecules of these substances. In order to make possible the consideration of the effect of each electron, it is assumed that this effect is equivalent to that which would result if the electron were located at some fixed point. The locations of these points with reference to the positive nuclei determine the electric moment of the molecule. Since these points will be spoken of as if they were the actual locations of the electrons, the method of considering the structure of the molecule will be similar to that employed by Lewis ‡ Langmuir §, and J. J. Thomson ||.

The positions of the centres of gravity of the positive and negative charges in a molecule are obtained in much the same way that the centre of gravity of a system of rigid bodies is located. The space coördinates, x, y , and z , of each positive charge are determined with reference to a conveniently located set of axes. If x, y , and z are the coördinates of the centre of gravity of the positive charges, e the value of the electronic charge $= 4.774 \times 10^{-10}$, and E the sum of all the positive charges in the molecule, then $\Sigma ex = E\bar{x}$, $\Sigma ey = E\bar{y}$, and $\Sigma ez = E\bar{z}$. The centre of gravity of the negative charges may be located by means of an analogous set of equations:

$$\Sigma ex' = E\bar{x}', \quad \Sigma ey' = E\bar{y}', \quad \Sigma ez' = E\bar{z}'.$$

The moment, μ , of the electric doublet thus located in the molecule is determined from its components,

$$\mu_x = E(\bar{x} - \bar{x}'), \quad \mu_y = E(\bar{y} - \bar{y}'), \quad \text{and} \quad \mu_z = E(\bar{z} - \bar{z}'),$$

which give

$$\mu = E \sqrt{(\bar{x} - \bar{x}')^2 + (\bar{y} - \bar{y}')^2 + (\bar{z} - \bar{z}')^2}.$$

* Communicated by the Author.

† C. P. Smyth, *Phil. Mag.* xlv. p. 849 (1923).

‡ G. N. Lewis, *Journ. Am. Chem. Soc.* xxxviii. p. 762 (1916).

§ I. Langmuir, *Journ. Am. Chem. Soc.* xli. p. 868 (1919).

|| J. J. Thomson, *Phil. Mag.* xli. p. 510 (1921).

The determination of the position of the centre of gravity of the electrons in a molecule is simplified by the justifiable assumption that the centre of gravity of the inner electrons of each atom is located in the nucleus of the atom and is never displaced from this position, only the electrons in the outer layer being displaced by external forces*. The application of this method of calculation to the hydrogen chloride molecule leads to the conclusion that the molecule may be regarded as an electric doublet, the axis of which is the line joining the two nuclei, and the moment of which is the product of one charge by the distance apart of the nuclei. From the infra-red absorption spectrum of hydrogen chloride† the internuclear distance is calculated as 1.265×10^{-8} cm. This gives for the moment of the HCl molecule, $\mu = 4.774 \times 10^{-10} \times 1.265 \times 10^{-8} = 6.039 \times 10^{-18}$, as compared with the value 2.15×10^{-18} obtained from the temperature variation of the dielectric constant of hydrogen chloride‡.

In this calculation of the moment from the internuclear distance, no account has been taken of the displacement of the outer electrons from their symmetrical locations by the attraction of the hydrogen nucleus. The force f necessary to produce unit displacement of an electron in a molecule may be calculated from the equation §

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi N e^2}{3f},$$

in which ϵ is the dielectric constant of the substance, N is the number of electrons in unit volume which suffer displacement, and e is the electronic charge. This equation is derived on the assumption that an electric doublet may be induced in the molecule by the external field, but that the molecule possesses no permanent doublet. The dielectric constant may then be taken as approximately equal to the square of the refractive index of the substance, provided this is taken for a spectral region which is sufficiently far removed from an absorption band. When the molecule possesses a permanent doublet, the true dielectric constant of the substance cannot be used in the equation, but the contribution of the induced doublet, which may be calculated as before from the square of the refractive index, may be

* J. J. Thomson, *loc. cit.*; M. Born and H. Kornfeld, *Phys. Zeits.* xxiv. p. 121 (1923).

† H. M. Randall, *Journ. Opt. Soc. Am.* vii. p. 45 (1923).

‡ H. Falkenhagen, *Phys. Zeits.* xxiii. p. 87 (1922).

§ N. R. Campbell, 'Modern Electrical Theory,' p. 34.

employed without introducing great error. N is obtained by multiplying the number of electrons displaced in one molecule—eight in the case of hydrogen chloride—by 2.705×10^{19} , the number of molecules in unit volume of the gas under standard conditions, to which the results of the measurement are reduced.

In the equation which has been given it is assumed that, when an electron is displaced, it is acted upon by a restoring force which is proportional to the displacement, and is therefore equal to fx , where x is the displacement. If the positive charge of the hydrogen nucleus in the HCl molecule attracts an electron according to the inverse square law, it will exert a displacing force upon the electron equal to $\frac{e^2}{d^2}$, where d is the distance apart of the two charges. Each of the outer electrons will be displaced toward the hydrogen nucleus, and, in order that there may be equilibrium in the new positions, the following relation must hold for each electron :

$$fx = \frac{e^2}{d^2}.$$

In the HCl molecule the centre of gravity of the electrons would be at a distance of 1.265×10^{-8} cm. from the hydrogen nucleus if no distortion occurred. If one electron at this distance from the hydrogen nucleus were displaced a distance x toward it by the force of attraction, the distance apart of the charges would be $(1.265 \times 10^{-8} - x)$ cm., and equilibrium would result when

$$fx = \frac{e^2}{(1.265 \cdot 10^{-8} - x)^2}.$$

Since f may be calculated from the refractive index of hydrogen chloride as $.71 \times 10^6$, the equation becomes

$$x(1.265 \cdot 10^{-8} - x)^2 = .322 \cdot 10^{-24}.$$

There is no solution of this equation for any value of x between 0 and $1.265 \cdot 10^{-8}$, which indicates that there should be no position of equilibrium between these values. In other words, the hydrogen nucleus should draw the electron to it. At least two of the electrons in the outer layer of the undistorted HCl molecule must be less than $1.265 \cdot 10^{-8}$ cm. from the hydrogen nucleus, and should therefore be attracted to it more readily than an electron at the distance for which the calculation has been made. Such an occurrence would be contrary to the generally

accepted ideas of atomic structure, and may be regarded as out of the question.

If a hydrogen nucleus could be attached to an argon atom, the resulting structure should resemble that of hydrogen chloride except for the presence of one more positive charge on the argon nucleus. From the value $f = 1.13 \times 10^6$ for argon, it may be calculated that a hydrogen nucleus at a distance of 1.265×10^{-8} cm. would displace an electron a distance of 0.169×10^{-8} cm. toward it. The displacement of eight electrons by a similar amount would approximately neutralize a moment equal to that calculated for the undistorted HCl molecule. If eight electrons in the outer shell of an atom are located at the corners of a cube, the diagonal of a face of which is 2×10^{-8} cm., and a hydrogen nucleus is located at a distance of 1.33×10^{-8} cm. from the nucleus of this atom on a line drawn from the nucleus at the centre of the cube through the mid-point of one edge, the displacement of each electron may be calculated for a given value of f . If f has the value 4.66×10^6 , as calculated for the neon atom, the total effect of the displacement of the electrons is sufficient to reduce by 11.8 per cent. the moment which the structure would have if undistorted. The value of f here used is undoubtedly too large for this structure, which means that the actual decrease in moment would be considerably larger than 11.8 per cent. in a structure of this character.

We are confronted by the difficulty that the use of the inverse square law and the values of f calculated from the refractive index leads commonly to the impossible result that the positive charge should draw the nearer electrons directly to it. In using these values of f , it must be borne in mind that they are only average values, and that the values are presumably not the same for all the displaceable electrons in a polyatomic molecule. Furthermore, the restoring force might be expected to depend upon the direction of the displacement, and no account is taken of this. In a detailed treatment of the electronic structure of the molecule, Thomson has found it necessary to use a radical modification of the inverse square law, other investigators also having followed a similar course. In view of these facts, it is not surprising that the attempted calculations of the displacements of the electrons in the molecules have failed to account quantitatively for the discrepancies between the observed and the calculated moments of the molecules; but these displacements are clearly of such an order of magnitude that they may be regarded as the main

cause of the discrepancies observed. It will presently appear that there is a connexion between the value of f and the amount of discrepancy.

Although there is some uncertainty as to the accuracy of the absolute values obtained for f due to the approximate character of the equations used in the calculations, the values should represent fairly well the relative ease of displacement of electrons in different molecules. The following table shows that f varies for different substances in the manner which would be predicted :—

TABLE I.

Substance.	Molecular formula.	Number of displaceable electrons.	$f \times 10^{-6}$.
Neon	Ne	8	4.66
Argon	Ar	8	1.13
Krypton	Kr	8	0.75
Xenon	Xe	8	0.46
Fluorine	F ₂	14	2.82
Chlorine	Cl ₂	14	0.72
Bromine	Br ₂	14	0.49
Iodine	I ₂	14	0.29
Hydrogen chloride	HCl	8	0.71
Hydrogen bromide	HBr	8	0.55
Hydrogen iodide	HI	8	0.35
Methane	CH ₄	8	0.71
Ammonia	NH ₃	8	0.84
Water	H ₂ O	8	1.24
Hydrogen sulphide	H ₂ S	8	0.51
Oxygen	O ₂	12	1.73
Sulphur dioxide	SO ₂	12	1.07

For the rare gases and the halogens, f decreases with increase in atomic weight, which is accompanied by increase in radius—that is, the electrons are more easily displaced the greater their distance from the positive nucleus. This effect appears to be analogous to the electromotive behaviour of the alkali and alkaline earth metals, which show increasing electrode potential as the size of the atom increases, making greater the distance of the outer electrons from the positive nucleus, and thereby increasing the ease with which these electrons leave the atom. If the values of f for the rare gases, the halogens, or the hydrogen halides are plotted as ordinates against the atomic or molecular weights as abscissæ, smooth curves are obtained which fall rapidly at the beginning, thereby calling to mind the rapid rise in this region of the atomic volume curves for the rare gases, the halogens, and the alkali metals. The agreement between

the values of f for the outer electrons of the halogen molecules and those for the electrons in the octets of the hydrogen halides would seem to offer evidence that the method of calculation employed involves no serious errors. The electrons in the halogen atoms are somewhat more easily displaced than are those in the corresponding rare gas atoms, which might be expected in view of the smaller nuclear charge of the halogens; but the situation is complicated by the fact that one pair of electrons is shared in both the halogen and the hydrogen halide molecules. The same is true in the case of the water, ammonia, and methane molecules, in which the increasing ease of displacement of the electrons may be due not only to the decreasing nuclear charge, but in part also to the increased number of shared pairs. Unfortunately, data are not available upon hydrogen fluoride.

If there were eighteen displaceable electrons in the krypton and xenon atoms and seventeen in the bromine and iodine atoms, as necessitated by Langmuir's theory of the structure of the heavy atoms, there would be a sharp increase in f on going from argon to krypton and from chlorine to bromine, followed by a decrease on going to the last member of each series. As there appears to be no explanation for such behaviour, and as there is good reason to expect the uniform decrease obtained when the number of displaceable electrons in the atom is assumed to be eight, this appears to give evidence in favour of a maximum number of eight electrons in the outer layer of the atom, which is in accord with the theories of Bohr and Thomson and with the modification of the Langmuir theory proposed by Bury*.

The structure of the water molecule proposed by Langmuir is a cubical arrangement of the electron octet formed by the sharing of the single electrons of the two hydrogen atoms with the six electrons in the outer shell of the oxygen atom, the two hydrogen nuclei being held at the centres of diagonally opposite edges of the cube. This symmetrical arrangement of the hydrogen nuclei fails to account for the pronounced dipolar character of the water molecule, and to explain this, Cuy† uses the tetrahedral arrangement of the octet proposed by Lewis. The location of the two hydrogen nuclei at apices of a tetrahedron produces an unsymmetrical molecule which should be dipolar. Thomson obtains the necessary lack of symmetry by assuming that the electrons

* C. R. Bury, *Journ. Am. Chem. Soc.* xliii. p. 1602 (1921).

† E. J. Cuy, *Zeits. f. Elektrochem.* xxvii. p. 371 (1921).

lie at the corners of a structure made by twisting one face of a cube through an angle of 45° without changing its plane.

If Langmuir's theory requires that the two hydrogen nuclei be attached always to diagonally opposite edges of the cube in the water molecule, thus giving a structure which would have no moment, the fact that the experimentally determined value of the moment of the water molecule is 1.87×10^{-18} * shows that the cubical structure is impossible in this case, and, by analogy, it becomes highly improbable in the case of the other light atoms, such as carbon, nitrogen, fluorine, and neon. Similarly, Langmuir's theory applied to hydrogen sulphide leads to a symmetrical structure analogous to that of the water molecule and having no moment. The value of the moment, 1.02×10^{-18} , calculated from experimental data † shows this to be impossible, and therefore argues against the cubical structure not only for sulphur, but also for the elements standing near it in the periodic system.

Although Langmuir assumed that the hydrogen nuclei are located only on diagonally opposite edges of a cube, it appears not impossible that other arrangements of these nuclei may exist. The location of the two nuclei on opposite edges of one face would give a molecule strongly dipolar in character, and their location on non-adjacent edges of two adjacent faces would give a molecule somewhat less strongly dipolar in character. If distortion of the cube is disregarded, it may be calculated by the method already described that the electric moment of a molecule with the hydrogen nuclei attached to diagonally opposite edges is 0, the moment of the molecule with the nuclei on opposite edges of the same face is $1.41 \epsilon p$, where ϵ is the electronic charge and p is the distance of each hydrogen nucleus from the oxygen nucleus, and the moment of the molecule with the nuclei on non-adjacent edges of two adjacent faces is ϵp . If water consisted of a mixture of these three different types of molecules, its pronounced dipolar character would be accounted for.

If ammonia had a cubical structure and the hydrogen nuclei were attached symmetrically to edges of three different faces of the cube and in no case to two edges of the same face, the molecule would have practically zero moment. The value for the electric moment of the ammonia molecule

* M. Jona, *Phys. Zvts.* xx. p. 14 (1919).

† C. P. Smyth, *loc. cit.*

calculated by Jona from experimental data is 1.53×10^{-18} . It might therefore be assumed, as in the case of the water molecule, that some at least of the ammonia molecules have an unsymmetrical structure in which two hydrogen nuclei are attached to opposite edges of one face of the cube. Such a structure, if there were no distortion, should have a moment equal to ep , where e and p have the same significance as in the case of the water molecule. The pronounced dipolar character of the ammonia molecule would thus be accounted for.

It is thus evident that if the molecular structures of water and ammonia are cubical, they cannot all be symmetrical. Some at least must be unsymmetrical in order to produce the electric moments which have been observed, and because of the large decrease in moment produced by displacement of the electrons in the unsymmetrical molecules it can readily be shown that these molecules would have to constitute a large fraction of the mixture in order to give an average moment as large as that observed. On the other hand, it is only reasonable to suppose that, because of the mutual repulsion of the hydrogen nuclei, the majority of the molecules would tend to be symmetrical and without moment. As a sufficiently large proportion of unsymmetrical molecules appears improbable in view of the tendency toward the formation of the symmetrical molecules, the cubical structure appears improbable.

The situation is much simpler if it is assumed that the electrons act as if located in pairs at the corners of a regular tetrahedron. An attempt was made to use the values for the principal moments of inertia of the water molecule calculated by Eucken * from the infra-red absorption spectrum to distinguish between the cubical and the tetrahedral structures for this molecule. Although the three principal moments of inertia calculated for the water molecule show that water cannot consist entirely of symmetrical cubical molecules and point toward the tetrahedral structure, they do not preclude the possibility of the existence of a mixture of symmetrical and unsymmetrical cubical molecules. It appears that the crystal structures of certain solids as revealed by X-rays give evidence in favour of a tetrahedral atomic structure †. The twisted cube proposed by Thomson gives an unsymmetrical structure which our present

* Eucken, A., *Jahrbuch d. Radioaktivität u. Elektronik*. xvi. p. 408 (1919-1920).

† M. L. Huggins, *Journ. Phys. Chem.* xxvi. p. 601 (1922); cf. R. G. Dickinson, *Journ. Am. Chem. Soc.* xlv. p. 958 (1923).

knowledge of electric moments does not serve to distinguish definitely from the tetrahedral structure. In view of the improbability of the cubical structure for the molecules which have been considered and the simplicity of the treatment required for the tetrahedral structure, this latter will generally be used in calculating the moments of molecules in the following paragraphs.

In order to test the value of the electric moment as an indication of the molecular structure, it is of interest to compare the observed and calculated values for the moments of molecules of related substances. It has been calculated * that the volumes of the carbon, nitrogen, and oxygen octets in methane, ammonia, and water respectively are practically identical, and that each hydrogen nucleus occupies approximately the same volume in all these molecules. It thus appears that the distance, p , of a hydrogen nucleus from the nucleus of the octet is approximately the same for the three different substances. If $p = 1.0 \times 10^{-8}$ cm., the values calculated for the moments on the assumption of a tetrahedral structure are $1.155 ep = 5.51 \times 10^{-18}$ for water, $ep = 4.77 \times 10^{-18}$ for ammonia, and 0 for methane; while the observed values are 1.87×10^{-18} , 1.53×10^{-18} , and a value less than 0.048×10^{-18} † respectively. The agreement between the observed and the calculated values for methane is satisfactory, and the discrepancies for the other two substances are of the same order of magnitude as that found in the case of hydrogen chloride. In the methane molecule the four pairs of electrons attracted by the hydrogen nuclei must suffer equal displacements so that the symmetry of the molecule is not altered and the moment remains zero. The ratio between the calculated values of water and ammonia is 1.155 and that between the observed values is 1.28, indicating that distortion of the electron positions has a slightly greater effect in reducing the moment of the ammonia molecule than it has in the case of the water molecule. This agrees with the fact that f for ammonia is 0.84×10^6 , while f for water is 1.24×10^6 , showing greater ease of displacement for the electrons in the ammonia molecule.

Hydrogen sulphide, presumably, has a structure analogous to that of water, and should therefore, if there were no distortion, have a moment equal to $1.155 ep$, or 6.89×10^{-18} , where p is taken equal to 1.25×10^{-8} cm. as compared with

* R. N. Pease, *Journ. Am. Chem. Soc.* xliii, p. 491 (1921).

† H. Riegger, *Ann. d. Phys.* lix, p. 753 (1919).

1.0×10^{-8} in the case of water *. However, instead of being larger than the moment of the water molecule as this would seem to indicate, the value calculated from the experimental data is 1.02×10^{-18} as compared with 1.87×10^{-18} for water. This seeming contradiction is explained by the fact that f for hydrogen sulphide is 0.51×10^6 as compared with 1.24×10^6 for water, showing that the electrons are much more easily displaced in hydrogen sulphide than in water, so that the displacement of the electrons makes a much greater decrease in the moment of hydrogen sulphide than it does in that of water, with the result that the moment of hydrogen sulphide is actually the smaller of the two.

The sulphur dioxide molecule was supposed by Langmuir to consist of a cubical sulphur atom sharing a face with one oxygen atom and an edge with the other oxygen atom. This structure may be represented by the formula $O=S^{-0}$, in which each line represents a pair of electrons shared between two atoms. If we assume, as approximate dimensions for the atoms in the molecule, 1.25×10^{-8} cm. for the radius of the sulphur and 1.0×10^{-8} cm. for the radius of the oxygen, the moment of this structure may be calculated as about 8.8×10^{-18} , considerably larger than the calculated value, 5.51×10^{-18} , for the water molecule; while the values observed, 1.76×10^{-18} by Jona and 1.87×10^{-18} by Falkenhagen, are approximately the same as that found by Jona for water. The ease of displacement of the electrons in the sulphur octet accounts for the great decrease in the moment of sulphur dioxide. The significance of the value of f , 1.07×10^6 , for the outer eighteen electrons of the sulphur dioxide molecule is diminished by the rather complicated distribution of these electrons between the sulphur and the oxygen atoms, and cannot be greatly emphasized; but it is apparent that the value of f for sulphur dioxide stands between those for water and hydrogen sulphide, as is also the case with the relative decrease in the moment due to displacement of the electrons. From viscosity measurements, Rankine and Smith † have calculated the mean area for molecular collisions of the sulphur dioxide molecule as 0.94×10^{-15} cm.², and have further calculated that a molecule of the structure $O=S^{-0}$ would have an area

* The values used for p in this paper are approximations based upon atomic dimensions as determined from moments of inertia, X-ray measurements, and the kinetic theory of gases.

† A. O. Rankine and C. J. Smith, Proc. Phys. Soc. London, xxxv. p. 33 (1922).

$1.08 \times 10^{-15} \text{ cm.}^2$; while, if the molecule had a ring

structure, $\text{S} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$, the area would be $0.99 \times 10^{-15} \text{ cm.}^2$, the

conclusion being that the latter is the more probable structure. The electric moment calculated for this structure is practically zero, while that calculated for the first structure is, as has been shown, in accord with the experimental facts. It seems impossible that a structure which would have practically zero moment can be correct for the molecule of a substance which has one of the largest moments yet observed experimentally. Cubical structures have been employed in these calculations for the sulphur dioxide molecule, but the assumption of tetrahedral structures would lead to essentially the same results.

Tetrahedral structures may be employed in the calculation of the moments of the molecules of alcohols and ethers. It is found that the value of the moment depends upon the distances of the hydrogen nuclei from the oxygen and the carbon nuclei. If these distances are a and b respectively, the moment of methyl alcohol may be calculated as

$$\mu = e \sqrt{(.943 a)^2 + (.999 b - .333 a)^2}.$$

It was indicated that the distance, ρ , of the hydrogen nuclei from the nuclei of the octets was approximately the same in the methane, ammonia, and water molecules. It might be argued from this that a would equal b , and that a and b would differ little from ρ . If $a=b=\rho$, $\mu = 1.155 e\rho$, which is the calculated value of the moment of the water molecule. The value of the moment calculated for ethyl alcohol is identical with that for methyl alcohol, and consideration of the geometrical structures assumed for these compounds reveals the fact that, if distortion is neglected, an alkyl group may be substituted for a hydrogen without affecting the moment of the molecule, which means that not only the acyclic saturated alcohols, but also the ethers, should all have the same moment as water. It would appear that the more complex structure attached to the oxygen in an alcohol molecule might give greater opportunity for decrease in the moment by electronic displacement than that occurring in the water, while the decrease in an ether molecule might be somewhat greater than that in an alcohol molecule.

The comparison of calculated and observed values is complicated in the case of the alcohols by molecular association, which makes difficult the calculation of the true value of the

moment from data upon the substance in the liquid condition. From values of the dielectric constant of methyl alcohol vapour at various temperatures, Jona calculated the moment of the molecule to be 1.61×10^{-18} as compared with 1.87×10^{-18} obtained for water in a similar manner. In a previous paper already referred to, the writer has used a different method to calculate the moment of methyl alcohol from Jona's data, obtaining values which, although varying slightly with temperature, indicate a moment of about 1.78×10^{-18} . The same method of calculation applied to the values of the dielectric constants obtained by Abegg and Seitz* gives a value of 1.70×10^{-18} for the ethyl alcohol molecule in the liquid at 20° and 1.71×10^{-18} for the propyl alcohol molecule at the same temperature. These values are, presumably, somewhat low because of molecular association, but should indicate approximately the magnitudes of the moments of these molecules. The moment of the ethyl ether molecule was calculated by Isnardi and Gans† from dielectric constant data on the liquid as 1.435×10^{-18} , and the calculations made by the writer from their data and from the data of Bädcker‡ on ether vapour agree well with this figure. Rather limited data obtained by Bädcker on the dielectric constant of gaseous methyl ether make possible a rough calculation of the moment of this molecule as about 1.3×10^{-18} . Too much significance cannot, however, be attached to this figure. It is apparent that the moments of the alcohol and ether molecules which have been investigated are close to the moment of water, thus agreeing with the conclusions arrived at from considerations of structure.

The moments of the chlorine substitution products of methane may be calculated, the displacement of the electrons being neglected. p is the distance of the hydrogen nuclei from the carbon nucleus, and r and c the distances from the nuclei to the outermost electrons in the chlorine and carbon atoms respectively. The moment of the methane molecule is, as has been shown, practically zero, and the moment calculated for the carbon tetrachloride molecule is also zero, while the values obtained for methyl chloride, methylene chloride, and chloroform are, respectively, $e(r+p-c)$, $1.155 e(r+p-c)$, and $e(r+p-c)$. The results indicate that, if there were no displacement of the electrons, methyl chloride and chloroform would have moments not

* R. Abegg and W. Seitz, *Zeits. f. Phys. Chem.* xxix, p. 242 (1899).

† H. Isnardi and R. Gans, *Phys. Zeits.* xxii, p. 239 (1921).

‡ K. Bädcker, *Zeits. Phys. Chem.* xxxvi, p. 304 (1901).

far from that of hydrogen chloride. However, the more complicated structures of the methyl chloride and chloroform molecules may give greater opportunity for the decrease of the moment by displacement of electrons, so that the moments observed for these molecules might be expected to be somewhat lower than the value 2.15×10^{-18} observed for hydrogen chloride. Unfortunately, the necessary experimental data are not available for the calculation of the moment of methyl chloride, but the moment of chlorobenzene has been calculated by the writer in the paper already referred to as 1.42×10^{-18} , and, on account of the symmetry of the benzene structure *, the moment of the C_6H_5Cl molecule should not differ greatly from that of the CH_3Cl molecule. The moment of methylene chloride was calculated from data given in Landolt-Börnstein (fourth edition) as 1.65×10^{-18} , a value which, because of the limited range of the data, must be regarded as only approximate, in spite of the fact that its ratio to the value of the moment of chlorobenzene is very close to that indicated by structural considerations. The value obtained by Isnardi for the moment of the chloroform molecule is 1.26×10^{-18} , while Lertes † found 1.35×10^{-18} for the same quantity. The mean, 1.31×10^{-18} , is in fair agreement with the value, 1.42×10^{-18} , for chlorobenzene. From Isnardi's data on the dielectric constant of carbon tetrachloride, the moment may be calculated by the writer's method as 0.39×10^{-18} at 0° and 0.48×10^{-18} at 62° . The value obtained is small, but not as small as might be expected in view of the apparent symmetry of the carbon tetrachloride molecule. It is not certain that the equations used in calculating these values give great accuracy for small values of the moment. It appears, however, that the molecules of this series of compounds have electric moments of the approximate magnitude predicted on the basis of structure.

It has been stated that the moment of the chlorobenzene molecule is 1.42×10^{-18} . If there were no displacement of the electrons, the bromobenzene molecule should have a moment which would be to the moment of chlorobenzene approximately as the radius of the bromine atom is to that of the chlorine atom. However, f for hydrogen chloride is 0.71×10^6 , while f for hydrogen bromide is 0.55, the quantities being very similar for the Cl_2 and Br_2 molecules respectively. The displacement of the outer electrons will,

* Isnardi's (*Zeits. f. Phys.* ix. p. 152, 1922) data on the dielectric constant of benzene indicate that the moment of the molecule is negligible.

† P. Lertes, *Zeits. f. Phys.* vi. p. 257 (1921).

therefore, be greater in bromobenzene than in chlorobenzene, and the resulting decrease in moment will be greater. The value of the moment obtained by the writer from the data of Lertes upon the dielectric constant of bromobenzene is 1.39×10^{-18} , showing that the greater ease of displacement of the electrons decreases the moment to about the same value as that observed for chlorobenzene. This effect is analogous to the great decrease in the moment of hydrogen sulphide as compared with that of water, but the effect is much less marked here because the difference between the values of f for chlorobenzene and bromobenzene is much less than the difference in the case of water and hydrogen sulphide.

There are many gaps and undoubtedly many errors in the data which have been considered, and the nature of the problem renders a precise treatment impossible in the present state of our knowledge; but the approximate agreement obtained between the magnitudes of electric moments calculated from molecular structures and those calculated from experimental data shows that the value of the electric moment of a molecule may be taken as an indication of its structure, and, in so far as the spatial arrangement of the atoms in a molecule is dependent upon the electronic structure of the atoms, the value of the moment of the molecule may give evidence of this electronic structure. A method is thus provided for obtaining evidence as to the arrangement of the atoms in the molecule of a substance.

The writer wishes to express his indebtedness to Professor K. T. Compton for his helpful advice and criticism.

Summary.

A method has been described for the calculation of the electric moment of a molecule by calculating the location of the centres of gravity of the positive and negative charges in the molecule. The force necessary to produce unit displacement of an electron in the outer layer of a molecule has been calculated from the refractive indices of a number of substances in the gaseous state. By the use of this quantity and the application of the inverse square law to the attraction between positive and negative charges within the molecule, it has been shown that, although the inverse square law is not obeyed with any exactitude, the electrons suffer displacements from positions of symmetry sufficient to account for the difference between the values of the electric

moment calculated from the theoretical molecular structure and those calculated from experimental data.

It has been further shown that (1) the force binding the outer electrons in an atom varies in such a way among different elements as to point to a maximum number of eight electrons in the outer shell of the atom, thus agreeing with the theories of Bohr, Thomson, and Bury, but differing from that of Langmuir ; (2) the tetrahedral arrangement of electrons is more probable than the cubical in H_2O , H_2S , NH_3 , and the closely-related molecules ; (3) the ring

structure $\text{S} \begin{smallmatrix} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{smallmatrix}$ for sulphur dioxide is much less probable

than the structure $\text{O}=\text{S}^{\text{O}}$; (4) the observed moments of the alcohols, ethers, and chlorine substitution products of methane are in accord with the values indicated by their electronic structures.

XLVI. *A Note on the Thermodynamics of Thermionic Emission.* By C. DAVISSON, Ph.D. *

IN applying the principles of thermodynamics to the thermionic properties of hot bodies, it is customary to consider the reversible changes possible in a system comprising a hot body in equilibrium with an atmosphere of electrons inside an enclosure (cylinder and piston) whose walls are impervious to electrons. This system differs in one important respect from the similar system of an enclosure containing an ordinary vapour in equilibrium with a condensed phase. The electrons being charged—or being charges—the establishment of the electron atmosphere within the enclosure is accompanied by the establishment of an electric field, and the system comes to equilibrium with the gaseous electrons distributed non-uniformly through the free space. This introduces a complication which is not present in the case of an ordinary saturated vapour. It is no longer permissible, in general, to write down a constant n as the number of particles per unit volume, nkT as the pressure against the walls of the enclosure, or $n\Delta r$ as the increase in the number of gaseous particles in the system during an isothermal expansion Δr .

The usual procedure in treating the problem has been to avoid these difficulties by assuming that the temperature

* Communicated by the Author.

of the system is kept so low during the reversible changes that no very great number of electrons is present in the gaseous state *. The intensities of the electric field approach zero as the space-charge is reduced, assuming the net charge of the system zero, and at sufficiently low temperatures the gaseous electrons will be almost uniformly distributed. It is assumed in the simple argument that all changes take place at temperatures for which the variations in electron density may be disregarded. With this limitation the problem becomes exactly that of an ordinary saturated vapour, and one arrives at the conclusion that the pressure of the vapour (molecular or electronic) will be given by

$$p = AT\epsilon^{\int \frac{\omega dT}{kT^2}}, \dots \dots \dots (1)$$

where A is a constant, ω the work required to transfer a single particle from the condensed to the gaseous state, and k is Boltzmann's gas constant. This result is combined in the thermionic problem with a theorem of the kinetic theory to give

$$i = A'T^{1/2}\epsilon^{\int \frac{\omega dT}{kT^2}} \dots \dots \dots (2)$$

as the relation between T and i , the current density of emission.

Strictly speaking, one should carry over into the conclusion in the electrical problem the temperature restriction used in the argument; the emission should be given by equation (2), provided T is not greater than that fixed as a permissible maximum in the argument. While there is not much question as to the correctness of the usual extrapolation to higher temperatures, it will perhaps put the deduction on a more satisfactory basis to present it in a form in which the temperature restriction is entirely avoided.

Let us imagine a system of two plane parallel surfaces; one on the left that emits electrons thermionically into the region between the two surfaces, and one on the right that is a perfect reflector of electrons and is non-emitting. If the system is uncharged when cold, then when raised to a high temperature an atmosphere of electrons is built up between the two surfaces, and the emitting surface is left with a positive charge equal in magnitude to the negative charge of the electron atmosphere. The system is a charged condenser, and in considering the changes that are possible in the

* O. W. Richardson, 'Emission of Electrons from Hot Bodies,' Chap. II.

system it will be necessary to take the energy of this charged condenser into account. The total charge of the electron gas per unit area of the emitting surface will be represented by E , and the total electrostatic energy per unit area by W .

We may imagine that the emitting surface coincides with the $x=0$ plane of a system of three rectangular coordinates. The reflecting surface then coincides with the $x=X$ plane, where X is the distance between the surfaces.

The charge per unit area of the system to the right of a plane x , ($0 < x < X$), is integral σdx from x to X , where σ represents charge density, and the charge per unit area to the left of this plane, including the charge on the emitting surface, is equal in magnitude but opposite in sign. The electric intensity at x is therefore

$$\frac{dV}{dx} = 4\pi \int_x^X \sigma dx. \quad . \quad . \quad . \quad . \quad (3)$$

At the reflecting surface the intensity is zero, so that the only force acting on this surface is that due to the gas-pressure of the electron at $x=X$.

We suppose the system capable of reversible transformation in T and X . It is required, therefore, on thermodynamical principles to satisfy Clausius' relation, which for present requirements may be written $\partial p / \partial T = \lambda / T$, where p is the pressure against the reflecting surface and λ is the latent heat of isothermal expansion per unit area of the system. To evaluate λ we have that during an isothermal expansion ΔX the number of gaseous electrons per unit area of the system is increased by $(\Delta X / e) \partial E / \partial X$, where e is the charge of one electron, and that this multiplied by ω is the quantity of heat absorbed by the transfer of these electrons from the metal to the electron atmosphere. A quantity of heat $(\partial W / \partial X) \Delta X$ is absorbed in increasing the electrostatic energy of the system, and a quantity $p \Delta X$ is absorbed by the system in doing work against external forces. Assuming that heat is absorbed in no other way, we have that the quantity absorbed per unit area of the system per unit change in X is $(\omega / e) \partial E / \partial X + \partial W / \partial X + p = \lambda$, and Clausius' equation becomes

$$\frac{\partial p}{\partial T} = \frac{1}{T} \left[\frac{\omega}{e} \frac{\partial E}{\partial X} + \frac{\partial W}{\partial X} + p \right]. \quad . \quad . \quad . \quad . \quad (4)$$

Since the electrons between the two surfaces are in a state of thermal equilibrium, we have by Boltzmann's relation

$\log \sigma + V_e/kT = \text{const.}$, or $dV_e/dx = -(kT/e)\sigma dx$. Combining this with equation (3), we find that σ satisfies the equation

$$\frac{d\sigma}{dx} = -\frac{4\pi e}{kT} \sigma \int_x^X \sigma dx.$$

The solution of this equation, supplied to me by Dr. T. C. Fry of this laboratory, is

$$\sigma = \sigma_1 \sec^2 \left[\frac{2\pi e \sigma_1}{kT} \right]^{1/2} (X-x), \quad \dots (5)$$

where σ_1 is a constant.

The same distribution law has been given in somewhat different form by v. Laue*, and Schottky† has deduced the law of distribution of potential for the same case. Equation (5) may be readily derived from either of these results.

At $x=X$, $\sigma=\sigma_1$, so that σ_1 represents the charge density at the reflecting surface, and the pressure against this surface is $p=\sigma_1 kT/e$. Writing σ_0 for the charge density at the emitting surface,

$$\sigma_0 = \sigma_1 \sec^2 \mu X, \quad \dots (6)$$

where $\mu^2 = 2\pi e \sigma_1 / kT$.

The total space-charge per unit area of the system is

$$\begin{aligned} E &= \sigma_1 \int_0^X \sec^2 \mu(X-x) dx \\ &= (\sigma_1 / \mu) \tan \mu X. \end{aligned}$$

Or, combining this with (6),

$$E = \sigma_1^{1/2} (\sigma_0 - \sigma_1)^{1/2} / \mu = [kT(\sigma_0 - \sigma_1) / 2\pi e]^{1/2}. \quad (7)$$

The density of electrostatic energy at x is

$$\frac{1}{8\pi} \left(\frac{dV}{dx} \right)^2 = 2\pi \left(\int_x^X \sigma dx \right)^2 = (2\mu \sigma_1^2 / \mu^2) \tan^2 \mu(X-x);$$

so that

$$\begin{aligned} W &= \frac{2\pi \sigma_1^2}{\mu^2} \int_0^X \tan^2 \mu(X-x) dx \\ &= (2\pi \sigma_1^2 / \mu^3) (\tan \mu X - \mu X). \end{aligned}$$

Or, combining this with (6) and (7),

$$\begin{aligned} W &= (2\pi \sigma_1^{3/2} / \mu^3) [(\sigma_0 - \sigma_1)^{1/2} - \mu \sigma_1^{1/2} X] \\ &= (kT/e) (E - \sigma_1 X). \quad \dots (8) \end{aligned}$$

* v. Laue, *Jahrb. der Rad. u. Elektronik*, xv. p. 205 (1918).

† Schottky, *ibid.* xii. p. 199 (1905).

We thus have expressions for ρ , E , and W in terms of T , X , σ_1 , and σ_0 . Differentiating these partially as required for substitution in (4), we find

$$\frac{\partial \rho}{\partial T} = \frac{k}{e} \left[\sigma_1 + T \frac{\partial \sigma_1}{\partial T} \right],$$

$$\frac{\partial E}{\partial X} = - \left[\frac{kT}{8\pi e} \right]^{1/2} \frac{\partial \sigma_1}{\partial X} / (\sigma_0 - \sigma_1)^{1/2},$$

and

$$\frac{\partial W}{\partial X} = - \frac{kT}{e} \left[\sigma_1 + X \frac{\partial \sigma_1}{\partial X} + \left(\frac{kT}{8\pi e} \right)^{1/2} \frac{\partial \sigma_1}{\partial X} / (\sigma_0 - \sigma_1)^{1/2} \right].$$

Substituting into (4) and collecting terms, we find that

$$-T \frac{\partial \sigma_1}{\partial T} = \left(\frac{kT}{8\pi e} \right)^{1/2} \left(1 + \frac{\omega}{kT} \right) \frac{\partial \sigma_1}{\partial X} / (\sigma_0 - \sigma_1)^{1/2} \\ + \left(\sigma_1 + X \frac{\partial \sigma_1}{\partial X} \right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We next differentiate (6) partially with respect to T and X , obtaining

$$\frac{\partial \sigma_0}{\partial T} = \frac{\partial \sigma_1}{\partial T} \sec^2 \mu X + \mu X \left(\frac{\partial \sigma_1}{\partial T} - \frac{\sigma_1}{T} \right) \sec^2 \mu X \tan \mu X \\ = \frac{\sigma_0}{\sigma_1} \left[\frac{\partial \sigma_1}{\partial T} + \left(\frac{2\pi e}{kT} \right)^{1/2} \left(\frac{\partial \sigma_1}{\partial T} - \frac{\sigma_1}{T} \right) (\sigma_0 - \sigma_1)^{1/2} X \right]$$

and

$$\frac{\partial \sigma_0}{\partial X} = 0 = \frac{\partial \sigma_1}{\partial X} \sec^2 \mu X + \mu X \left(\frac{\partial \sigma_1}{\partial X} + \frac{2\sigma_1}{X} \right) \sec^2 \mu X \tan \mu X \\ = \frac{\partial \sigma_1}{\partial X} + \left(\frac{2\pi e}{kT} \right)^{1/2} \left(\frac{\partial \sigma_1}{\partial X} + \frac{2\sigma_1}{X} \right) (\sigma_0 - \sigma_1)^{1/2} X.$$

Solving these for the $\partial \sigma_1 / \partial T$ and $\partial \sigma_1 / \partial X$, gives

$$\frac{\partial \sigma_1}{\partial T} = \left[\frac{\sigma_1}{\sigma_0} \frac{\partial \sigma_0}{\partial T} + \left(\frac{2\pi e}{kT} \right)^{1/2} \frac{\sigma_1 X}{T} (\sigma_0 - \sigma_1)^{1/2} \right] \\ \div \left[1 + \left(\frac{2\pi e}{kT} \right)^{1/2} X (\sigma_0 - \sigma_1)^{1/2} \right]$$

and

$$\frac{\partial \sigma_1}{\partial X} = - \left(\frac{8\pi e}{kT} \right)^{1/2} \sigma_1 (\sigma_0 - \sigma_1)^{1/2} / \left[1 + \left(\frac{2\pi e}{kT} \right)^{1/2} X (\sigma_0 - \sigma_1)^{1/2} \right].$$

On substituting these into (9), the equation is found to reduce to

$$\frac{1}{\sigma_0} \frac{\partial \sigma_0}{\partial T} = \frac{\omega}{kT^2},$$

which integrates to

$$\sigma_0 = A \epsilon^{\int \frac{\omega dT}{kT^2}}.$$

From this point the deduction follows the usual lines. The number of electrons per unit volume at the emitting surface is σ_0/e , and, by the theorem of the kinetic theory already referred to, the number striking unit area of the emitting surface in unit time is

$$N = \frac{\sigma_0}{e} \left(\frac{kT}{2\pi m} \right)^{1/2},$$

where m is the mass of the electron. If the coefficient of reflexion of the surface for electrons is zero, this is also the number emitted from unit area in unit time. The current density of emission is then given by

$$i = Ne = A \left(\frac{kT}{2\pi m} \right)^{1/2} \epsilon^{\int \frac{\omega dT}{kT^2}} = A' T^{1/2} \epsilon^{\int \frac{\omega dT}{kT^2}}.$$

We thus arrive at equation (2) without introducing a temperature restriction into the argument.

Research Laboratories of the
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and the Western Electric Company, Inc.
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XLVII. *The Halogen Hydrides.* By HERBERT BELL,
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Summary.

THE absorption-band spectra in the infra-red of the halogen hydrides HF, HCl, HBr have recently been determined very carefully by several investigators. In this paper the experimental data have been analysed with the aid of the energy-formula developed by Born and Hückel. It is shown that the values of the coefficients in the formula $1/\lambda = c_0 + c_1m + c_2m^2 + c_3m^3$ which embodies the experimental

* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

results for the main band and its overtones are, within the limits of experimental error, consistent with theory. The accuracy is not sufficient, however, to decide whether the "zero-point energy" exists or not.

The significance of the constants in the formula is discussed. Their determination makes it possible to evaluate the variation with distance of the force acting on the hydrogen nucleus as it vibrates along the line joining the two nuclei. The range of vibration for one, two, and three energy quanta is calculated.

THE HCl MOLECULE.

Spectral Data.

The infra-red absorption band of HCl at 3.5μ has recently been carefully investigated * by Colby, Meyer, and Bronk, and the wave numbers of the individual lines are found to be represented by

$$1/\lambda = 2886.07 + 20.60m - .301m^2 - .00206m^3, \quad (1)$$

where m has successive integral values from -19 to $+20$ excluding $m=0$, the missing central line.

From the earlier pioneer work of Imes † on the "overtone" at 1.76μ a least square formula may be obtained :

$$1/\lambda = 5667.0 + 20.14m - .558m^2 - .000086m^3. \quad (2)$$

The latter constants are, however, much less accurately determined, as there are only 16 lines $m=-8$ to $m=+8$ and the isotope lines also interfere.

General.

It is well known that these and similar band spectra represent quantum jumps of the molecule from a lower energy level to a higher one as light energy is absorbed. The molecular energy is in part due to oscillations along the line of join of nuclei, and in part to a rotation about an axis perpendicular to this line.

Various approximations to the mathematical solution of such a model have been given, and we may mention in particular those of Kratzer ‡ and of Born and Hückel §. We shall use the notation and formula developed by the latter investigators.

* Astroph. Journal, lvii. (Jan. 1923).

† Astroph. Journal, l. p. 251 (1919).

‡ Sommerfeld's *Atombau u. Spektrallinien*.

§ *Physik. Zt.* xxiv. (Jan. 1923).

Let the nuclei of the molecule when not oscillating or rotating be in equilibrium at a distance r_0 from each other, and let us suppose that the force function $U(r)$ along the line of join depends on r only and has derivatives U'_0 , U''_0 , etc., at this point. If, now, the molecule be given n radial quanta and m' rotational quanta, the energy W is, according to Born and Hückel, given by

$$W_m^n = U_0 + nh\nu_0 \left(1 + \frac{(\beta+3)\gamma^2}{2\nu_0^2} m'^2 \right) - n^2 h \delta + \frac{1}{2} h \gamma m'^2 - \frac{1}{2} h \gamma^3 m'^4 / \nu_0^2, \quad (3)$$

where the following abbreviations are used :

$$2\pi\nu_0 = \sqrt{U''_0/\mu}, \quad (4)$$

where μ is the reduced mass of the system and ν_0 is the frequency of small oscillations,

$$\beta = r_0 U_0''' / U_0'', \quad (5)$$

$$\gamma = h / 4\pi^2 \mu r_0^2, \quad (6)$$

$$\delta = 5\gamma / 48 (\beta^2 - 3r_0^3 U_0^{iv} / 5U_0''). \quad (7)$$

It is here understood that n may have any positive value, but may change only by integral steps from, say, n_0 to $n + n_0$, while m' may be either positive or negative, fractional or integral, but, according to the Correspondence Principle, may change only by unit steps, if at all. An equivalent statement for m' if it changes is that it can only *increase algebraically* to $m' + 1$. For if we imagine an observer looking in any direction, he will see molecules spinning both to left and right, m' positive or negative, but if he disregards all those whose angular momentum on changing does not increase in an algebraic sense, and leaves these to a second observer looking in the opposite direction who in turn disregards all others, then both observers will record only algebraic increase and will take into account all the molecules. From this point of view, negative values of m' correspond to molecules suffering an energy decrease.

Band Formulae.

The frequency of the absorbed light is now, by Bohr's principle, given by

$$\nu = (W_{m'+1}^{n+n_0} - W_{m'}^{n_0}) / h ;$$

and performing the necessary algebra we obtain

$$\nu = n \{ \nu_0 - 2n_0 \delta - (\beta+3)(m'+1)^2 \gamma^2 / 2\nu_0 - n \delta \} + (m' + \frac{1}{2}) \gamma \{ 1 + \gamma n_0 (\beta+3) / \nu_0 \} - 3\gamma^3 m'^2 / \nu_0^2 - 2\gamma^3 m'^3 / \nu_0^2. \quad (8)$$

The central missing line must be included in this; and assuming that it corresponds to a definite small value of m' , say m'_0 , and writing $m = m' - m'_0$, equation (8) becomes

$$\nu = c\nu_0 + m\gamma\{1 + \gamma(\beta + 3)[n_0 + n(m'_0 + 1)]/\nu_0\} \\ + nm^2\gamma^2\frac{(\beta + 3)}{2\nu_0}\left\{1 - \frac{3\gamma(m'_0 + 1)}{n\nu_0(\beta + 3)}\right\} - 2\gamma^2m^3/\nu_0^2, \quad (9)$$

$$\text{where } c\nu_0 = n\{\nu_0 - 2n_0\delta + \gamma^2(\beta + 3)(m'_0 + 1)^2/2\nu_0 - n\delta\} \\ + (m'_0 + \tfrac{1}{2})\gamma(1 + \gamma n_0(\beta + 3)/\nu_0) \quad (10)$$

is the frequency of the missing line, ($m = 0$).

[If m' does not change with n , then (8) is replaced by

$$\nu = (W_m^{n+n_0} - W_m^{n_0})/h \\ = n(\nu_0 - 2n_0\delta - n\delta) + nm'^2(\beta + 3)\gamma^2/2\nu_0,$$

a band without a centre which has not as yet been observed in the infra-red, but occurs frequently in the visible.]

Now Kratzer has given a formula for successive band centres, the n th one being expressed by

$$c\nu_0 = n(\tilde{\nu} - nx), \quad (11)$$

where x is a small quantity and ν is a constant. This formula has been verified in several cases as far as observational data allow. We notice that if the law holds exactly, then by (10) $m'_0 + \frac{1}{2} = 0$, so that the missing line denotes an absence of absorption, due to reversals in the molecule from an angular momentum of a half quantum to a half quantum in the opposite direction. This idea has several attractions. It endows the molecules permanently with at least a half quantum such as was demanded by Einstein and Stern* in the case of H_2 for the specific heat at low temperatures. The half quantum has also been found necessary by Kratzer† and by Curtis‡ for several bands in the visible. Furthermore we note that, as regards the energy of rotation, no increase is demanded for this reversal, and correspondingly no absorption of light-energy is to be expected.

Determination of Constants.

Leaving the point undecided for the present, we represent the bands in general by

$$\nu = c\nu_0 + c_1m + c_2m^2 + c_3m^3, \quad (12)$$

* *Ann. d. Phys.* xl. p. 551 (1913).

† *Ann. d. Phys.* lxxi. p. 72 (1923).

‡ *Proc. Roy. Soc. A*, ciii. p. 314 (1923).

where cc_0 is given by (10)

$$cc_1 = \gamma \{ 1 + \gamma(\beta + 3) [n_0 + n(m' + 1)]/\nu_0 \}, \quad \dots \quad (13)$$

$$cc_2 = n\gamma^2(\beta + 3)/2\nu_0 \left\{ 1 - \frac{3\gamma(m'_0 + \frac{1}{2})}{n(\beta + 3)\nu_0} \right\}, \quad \dots \quad (14)$$

$$cc_3 = -2\gamma^3/\nu_0^2. \quad \dots \quad (15)$$

A preliminary approximate verification of these formulæ is obtained at once by noting that $c_0^2 c_3 / 2c_1^3 = -n^2$ approximately. This is obtained by neglecting γ/ν_0 in comparison with unity, as can readily be seen to be legitimate on comparing (10), (12) . . . (15) with (1). Substituting values for the fundamental from (1), we therefore have $n^2 = \frac{1}{2}(2886)^2 \times .00206 / (20.6)^3 = .98$, showing that $n = 1$.

For the overtone $n = 2$ we cannot apply this test owing to inaccuracy in the determination of c_3 . By (15), in fact, the coefficient of m^3 should be the same in (2) as in (1), whereas (2) gives .000086 against .00206.

We easily find that approximately $\beta = -7$, for approximately

$$c_0 c_2 / c_1^2 = \frac{1}{2} n^2 (\beta + 3) (1 - n\delta/\nu_0) \div \{ 1 + 2(\beta + 3)\gamma n(m'_0 + 1)/\nu_0 \}$$

on neglecting squares of γ/ν_0 and taking $n_0 = 0$. Hence

$$\beta = -3 + \frac{2}{n^2} \frac{c_0 c_2}{c_1^2} \left(1 + \frac{n\delta}{\nu_0} \right) (1 + 2\gamma n(\beta + 3)(m'_0 + 1)/\nu_0). \quad (16)$$

Substituting from the fundamental, we have approximately

$$\beta = -3 - 2 \times 2886 \times .301 / (20.6)^2 = -7.1,$$

while the overtone gives $\beta = -3 - \frac{2 \cdot 5887 \times .588}{4 \cdot (20.1)^2} = -7.2$ in

excellent agreement. We shall take $\beta = -7$, and proceed to compare the c_1 's for the fundamental and overtone. From (1), (2), and (13) we have, on putting $n_0 = 0$, $\beta = -7.1$,

$$20.60c = \gamma(1 - 4.1\gamma(m'_0 + 1)/\nu_0),$$

$$20.14c = \gamma(1 - 8.2\gamma(m'_0 + 1)/\nu_0),$$

giving $\gamma = 41.20c - 20.14c = 21.0c$

and $.46c = 4\gamma^2(m'_0 + 1)/\nu_0$,

or $m'_0 + 1 = .75$; $m'_0 = -.25$

midway between the half quantum and the value zero usually assumed. A decrease in 20.14 to 19.98 would reduce m'_0 to zero. The band data, however, appear too definite for this.

Returning now to (10), we have approximately, on neglecting $(\gamma/\nu_0)^2$, with $n_0=0$

$$cc_0 = n(\nu_0 - n\delta) + \gamma(m_0' + \frac{1}{2}).$$

Substituting from (1) and (2),

$$\nu_0 - \delta = 2886 - 5 = 2881,$$

$$2\nu_0 - 4\delta = 5667 - 5 = 5662,$$

$$\text{or } \delta = 50c; \nu_0 = 2931c.$$

A second overtone is predicted at ($n=3$):

$$3\nu_0 - 9\delta + 5 = 8548; \lambda = 1.198\mu.$$

Using low resolving power, Schaefer * detected this band at approximately 1.190μ , which is perhaps in agreement within the limits of experimental error. It will be found that taking $m_0' + \frac{1}{2} = 0$ makes very little difference in the predicted position, 1.199μ instead of 1.198μ .

The Heat Band.

Colby, Meyer, and Bronk (*loc. cit.*) have also investigated the absorption of HCl at high temperatures ($500^\circ\text{C}.$), and have discovered five new lines belonging to the band of unit quantum absorption by molecules already possessing one quantum due to heat agitation. Whatever value m_0 may have for the fundamental, and we have assumed it to be zero, it is $n_0 + 1$ in this case, and consequently the expected centre cc_0 is by formula (10) displaced by $2\delta = 100c$ towards longer wave-lengths, i. e., $\bar{c}_0 = 2786$. At the same time, by (13) $\bar{c}_1$ is reduced relatively to c_1 of the fundamental by the factor $1 + \gamma(\beta + 3)/\nu_0 = .971$. Hence $c_1 = 20.60 \times .971 = 20.0$. c_2 and c_3 are unaffected, so that we may predict the formula

$$1/\lambda = 2786.0 - 20.0 m - .301m^2 - .00206m^3. \quad (17)$$

The following table shows the agreement between the observed lines and their positions as given by this formula:—

$m.$	ν (calc.).	ν (obs.).	Obs.—Calc.
— 9	2563.2	2759.7	3.5
— 10	2558.0	2554.7	3.3
— 11	2532.4	2528.8	3.6
— 12	2506.3	2502.1	4.2
— 13	2479.7	2476.0	3.7
			3.7

* *Zt. f. Phys.* (6) xii. p. 330.

The remaining lines are smothered by the main band which it overlaps, but in the open space of the fundamental at the missing line we might expect to uncover the heat band. The investigators in searching for grating "ghosts" found an irregularity "near the base of -1 ," *i. e.* > 2865 . Putting $m = +5$ in the above formula, we obtain 2879. A closer fit is obtained by adding 3.7cm.^{-1} to the formula, which is equivalent to reducing 2δ by this amount, *i. e.* from $100c$ to $96.3c$. To make this consistent with (10) and the previous calculation, m_0' requires to be -0.9 instead of -2.4 . It may confidently be predicted that further lines in this band will be of critical value in determining the band constants.

The Oscillation Constants.

Distance between the nuclei, r_0 . With $\gamma = 21.0 \times 3 \times 10^{10}$ and $h = 6.55 \times 10^{-27}$ we have from (6), on taking $\mu = 1.616 \times 10^{-24}$ gm.,

$$r_0 = 1.27 \times 10^{-8} \text{ cm.}$$

Natural frequency of small oscillations, ν_0 . With $m_0' = -2.4$ we have already obtained

$$\nu_0 = 2931c.$$

Indeterminateness in m_0' only slightly affects this value.

Returning to (16) with the above constants and $m_0' = -2.4$, we have from the 3.5μ band $\beta = -7.00$, while the less accurate formula for the overtone gives $\beta = -6.9$; we may therefore take

$$\beta = -7.00.$$

The Equation of Motion.

Assuming the molecule to be oscillating without rotation so that r_0 is the equilibrium distance and $U_0' = 0$, we have

$$\mu \ddot{x} = - \frac{d}{dx} U = - U_0'' x - \frac{1}{2} U_0''' x^2 - \frac{1}{6} U_0^{iv} x^3 - \dots \quad (18)$$

$$\text{or} \quad \ddot{x} = -k_1 x - k_2 x^2 - k_3 x^3 - \dots$$

Now, the solution of this equation has been given by Hettner* as

$$x = -\frac{1}{2} k_2 / k_1 A^2 + A \cos \phi t + \frac{1}{6} k_2 / k_1 A^2 \cos 2\phi t + \frac{1}{6} A^3 (k_2^2 / 3k_1^2 + k_3 / 2k_1) \cos 3\phi t + \dots$$

$$\text{where} \quad \phi = k_1^{1/2} \left(1 - \frac{5}{12} \frac{k_2^2}{k_1^2} A^2 + \frac{3}{8} \frac{k_3}{k_1} A^2 - \dots \right).$$

* *Zt. f. Phys.* i. p. 349 (1920).

On comparing coefficients of (18) and (19),

$$k_2/k_1 = U_0'''/2U_0'' = \beta/2r_0 \text{ by (5),}$$

$$k_3/k_1 = U_0^{iv}/6U_0'' = \frac{5}{18r_0^2}(\beta^2 - 48\delta/5\gamma) \text{ by (7).}$$

Equation (18) therefore becomes

$$\ddot{x}/4\pi^2\nu_0^2 = -r_0\{x/r_0 + \frac{1}{2}\beta(x/r_0)^2 + \frac{1}{18}(5\beta^2 - 48\delta/\gamma)(x/r_0)^3 - \dots\}, \quad (20)$$

having the solution, on writing η for A/r_0 ,

$$x/r_0 = -\frac{1}{4}\beta\eta^2 + \eta \cos \phi t + \frac{1}{12}\beta\eta^2 \cos 2\phi t + \frac{1}{72}(\beta^2 - 6\delta/\gamma)\eta^3 \cos 3\phi t - \dots, \quad (21)$$

with $\phi = 2\pi\nu_0(1 - \delta/\gamma\eta^2). \quad (22)$

To determine the constant A , we have the quantum condition

$$nh = \oint \mu \dot{x} dx = 2 \int_0^T \mu \dot{x}^2 dt, \quad (23)$$

where T is the half period of oscillation, so that

$$\phi T = \pi.$$

Now, from (21)

$$\dot{x}/r_0 = -\phi\eta\left\{\sin \phi t + \frac{1}{6}\beta\eta \sin 2\phi t + \frac{1}{24}(\beta^2 - 6\delta/\gamma)\eta^2 \sin 3\phi t - \dots\right\}$$

so that $\dot{x}^2$ involves products of the form $\sin p\phi t \sin q\phi t$ where p and q are integers. The integral of such products over a half oscillation vanishes except when $p=q$, in which case

$$\int_0^T \sin^2 p\phi t dt = \frac{1}{2}T = \pi/2\phi.$$

Hence, squaring $\dot{x}/r_0$ and substituting in (23), we have on integrating

$$nh/2\mu r_0^2 = \phi^2\eta^2 \frac{\pi}{2\phi} \left\{ 1 + \frac{\beta^2}{36}\eta^2 + \left(\frac{\beta^2 - 6\delta/\gamma}{24}\right)^2 \eta^4 - \dots \right\},$$

and on substituting from (22) and (6),

$$2n\gamma = \frac{nh}{2\pi^2\mu r_0^2} = \nu_0\eta^2 \left[1 - (\delta/\gamma - \beta/36)\eta^2 + \left\{ (\beta/24 - \delta/4\gamma)^2 - \frac{\beta\delta}{36\gamma} \right\} \eta^4 - \dots \right]$$

or

$$(\delta/\gamma - \beta/36)\eta^4 - \eta^2 + 2n\gamma/\nu_0 = \left(\frac{\beta^2}{576} + \frac{7}{144} \frac{\beta\delta}{\gamma} + \frac{\delta^2}{16\gamma^2} \right) \eta^6. \quad (24)$$

Range of Oscillation. Substituting in this equation $\delta=50c$, $\gamma=21\cdot0c$, $\beta=-7\cdot00$, $\nu_0=2931c$, and solving for η^2 , we have

$$\eta^2=(A/r_0)^2=\cdot0149, \cdot0308, \cdot0486,$$

$$A/r_0=\cdot122, \cdot176, \cdot220,$$

corresponding respectively to $n=1, 2, 3$.

To find the range of oscillation, we substitute $\phi t=0$ and $\phi t=\pi$ in (21) and subtract, giving

$$\text{Range}/r_0=2\eta\left(1+\frac{\beta^2-6\delta/\gamma}{72}\eta^2\right), \quad . \quad . \quad (25)$$

or on using the values of η given above, we find that the relative half amplitudes are

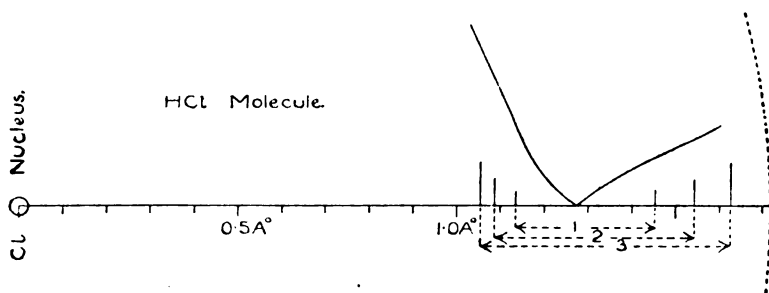
$$\cdot123, \cdot179, \cdot225.$$

Similarly, by adding instead of subtracting, we obtain for the relative displacement of the mean centre

$$\bar{x}/r_0=-\beta/6\eta^2, \quad . \quad . \quad . \quad (26)$$

having the respective values $\cdot017, \cdot036, \cdot057$. The oscillation centre is thus displaced by an amount proportional to the energy, a result * given by Debye.

Fig. 1.



These results are represented graphically in fig. 1. The Cl nucleus is represented as at rest and a scale of Ångström units attached. The relative field of force acting on the H nucleus when displaced is shown by the curve, which is calculated from (20) and drawn so that the height represents the restoring force. It brings out clearly the steepness of the gradient on the Cl side. The range of oscillation for the fundamental band and the overtones is also indicated.

* *Math. Vorlesungen an der Univ. Göttingen*, vi. p. 26.

THE HF AND HBr MOLECULES.

The band spectra for these molecules have not been nearly so well measured. From Imes's data for HF the least square formula can be derived

$$1/\lambda = 3962.5 + 40.34m - .76m^2 - .015m^3, \quad (27)$$

and for HBr

$$1/\lambda = 2559.2 + 16.52m - .23m^2 - .002m^3. \quad (28)$$

Using equation (16), we have approximately

$$\beta_{\text{HF}} = -6.7; \quad \beta_{\text{HBr}} = -7.3.$$

Assuming $m_0' = -.24$ as in HCl and applying (13), we have

$$\gamma_{\text{HF}} = 41.5c; \quad \gamma_{\text{HBr}} = 17.9c.$$

Hence, solving (6),

$$r_{0\text{HF}} = .97 \times 10^{-8} \text{ cm.}; \quad r_{0\text{HBr}} = 1.37 \times 10^{-8} \text{ cm.}$$

As regards the constant δ , which requires the exact centres of the overtones for its determination, we have only approximate values. For HF the overtone was observed by Schaefer (*loc. cit.*) at 1.27μ , i. e. $7.87 \times 10^3 \text{ cm}^{-1}$. For HBr, Brinsmeade and Kemble* obtained 1.98μ or $5.05 \times 10^3 \text{ cm}^{-1}$.

With these values and applying Kratzer's formula (11), we obtain x , which is approximately δ , as

$$\delta_{\text{HF}} = (27 \pm 5)c; \quad \delta_{\text{HBr}} = (34 \pm 5)c.$$

Since $\delta_{\text{HCl}} = 50c$ and the constants for HCl in other cases all lie intermediate between those of HF and HBr, we cannot regard these approximations with any confidence.

Neglecting δ and proceeding to an approximate solution of the motion, we have from (24)

$$\begin{aligned} \eta^2 &= A^2/r_0^2 = 2n\gamma/\nu_0 = .021 \text{ for HF,} \\ &= .0140 \text{ for HBr,} \\ &= .0143 \text{ for HCl.} \end{aligned}$$

The relative range of oscillation for HF is thus considerably larger than for the other two, due, of course, to the larger relative size of its quantum. The restoring force U_0'' for HF, HCl, and HBr near the position of equilibrium varies as $\mu\nu_0^2$ or

$$1.84 : 1 : .80.$$

* Proc. Nat. Acad. Wash. vol. iii, p. 420 (1918).

The corresponding relative variation of this with distance or U_0'''/U_0'' is

$$1.33 : 1 : .98.$$

It has already been pointed out * by W. L. Bragg and the writer that the progressive increase in nuclear separation for HF, HCl, HBr is very nearly equal to the corresponding increase in size of the atomic "radius" as determined by X-ray analysis. With the tentative atomic radii which Bragg had calculated, this led to the result that the H nucleus was in all cases at the same distance .26 angstroms from the halogen shell. Later work by Wasastjerna † has, as Professor Bragg has kindly pointed out to the writer, considerably modified these dimensions, although, of course, the X-ray nuclear distances are retained. The halogen atoms have all been increased by a constant quantity at the expense of other atoms. The radius of Cl^- , for example, has been increased from 1.05 angstroms to 1.72, its new radius being indicated in the figure by the outer circle. This value agrees closely with that given recently by Davey ‡. Examination of the scattering effects of NaCl by Bragg, James, and Bosanquet § has also shown that the effective shell of Cl^- ends between 1.6 and 1.8 angstroms. We may now therefore deduce that the H nucleus is well within the halogen shell, and is buried to the same depth for all three, HF, HCl, and HBr.

Fig. 2.

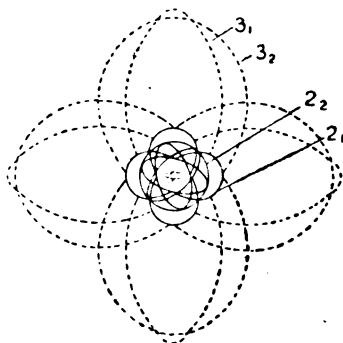


Fig. 2 represents the argon electron "economy" as given by Kramers || and reproduced with his kind permission.

* 'Nature,' March 24, 1921.

† *Commentationes. Physico-Math.* I. vol. xxxviii. *Soc. Scient. Fennica.*

‡ *Physical Review*, vol. xxii. (Sept. 1923).

§ *Phil. Mag.* xlv. p. 444 (1922).

|| *Naturwissenschaften*, 1923, p. 550.

We may take this as representing closely to scale the Cl^- atom, and identifying its outer orbits with the 1.72 angstrom sphere of fig. 1, we see that the inner neon shell has a radius of only about half an angstrom. Comparing the two figures then, we see that the oscillations of the H nucleus are always well outside the neon shell.

The author wishes to express his appreciation of the interest and encouragement shown by Professor W. L. Bragg in this work.

Physics Dept.,
University of Manchester,
Dec. 1923.

P.S.—Since writing the above, Mr. D. R. Hartree has kindly sent me the following note on the dimensions of the Cl^- ion:—

“Wasastjerna’s figure of 1.72 A.U. refers rather to the *apparent* size of this ion in crystals than to the actual dimensions of the orbits. It seems probable that any value of the apparent radius of an ion, derived either from the kinetic theory ‘diameter’ of the atom of the neighbouring inert gas (as Wasastjerna’s value is) or from the packing of monatomic ions in crystals (as is the case for Davey’s value) is only an upper limit for the real radius of the ion (defined as the radius of the smallest sphere enclosing all orbits of the ion).

“An estimate of this latter quantity can be obtained by an extension of the work of which an account is given in Proc. Camb. Phil. Soc. vol. xxi. Part 6, p. 625 (1923). The value 1.22 A.U. for the radius of the Cl^- ion in this sense has been given in a recent paper [Phil. Mag. vol. xlv. p. 1091 (1923)]; later work suggests that this value may be somewhat too low.

“The diagrams of orbits in Kramer’s paper (*Naturwissenschaften*, Heft 27, p. 550) are intended to be drawn approximately to scale, though it is not stated how the dimensions of orbits were obtained. Measuring up on this diagram, the radius of the argon atom appears to be about 1.15 A.U. From ionic refractivity Wasastjerna (*loc. cit.*) deduces the figure 1.20 for the ratio of the radius of Cl^- (in the present sense) to that of A, which gives 1.38 A.U. for the radius of the Cl^- ion.

“These estimates are both rather rough, but it seems likely that the radius of Cl^- is about 1.3 A.U.; if this value is correct, and if the ion were not distorted by the presence of the H nucleus, the latter would thus be situated about on the boundary of the ion.”

XLVIII. On the Law and Mechanism of the Emission of Electrons from Hot Bodies. By SURESH CHANDRA ROY, M.Sc., Research Scholar in Physics, University College of Science, Calcutta*.

INTRODUCTION.

THE law of dependence of thermionic currents on temperature was given first by Richardson† on the view that these currents were due to electrons shot out owing to the vigour of their thermal motions, and he adduced experimental evidence‡ in support of his conclusions. The deduction of his law was based on the supposition that the electrons, both outside and inside the hot body, were governed by the same laws of classical dynamics. On this supposition, he got the following expression for the thermionic current per unit area per sec. :

$$I = \int_{\left(\frac{e\phi}{m}\right)^{\frac{1}{2}}}^{\infty} ne x \left(\frac{m}{2\pi kT} \right)^{\frac{1}{2}} e^{-\frac{m}{2kT} x^2} dx, \quad \dots (1)$$

where ϕ is the work done during the transference of one electron from the hot body to the outside,

m = electronic mass,

e = electronic charge,

n = number of electrons per c.c., and

k = gas constant per mol.

On treating n as constant and independent of temperature,

$$I = A_1 T^{\frac{1}{2}} \cdot e^{-\frac{\phi}{kT}}, \quad \dots (2)$$

where

$$A_1 = ne \left(\frac{k}{2\pi m} \right)^{\frac{1}{2}}.$$

Here A_1 and ϕ are arbitrary constants independent of temperature, provided n be independent of temperature.

Richardson§ then showed on the basis of purely thermo-

* Communicated by Prof. C. V. Raman, M.A., D.Sc.

† Camb. Phil. Proc. ii. p. 286 (1901).

‡ Phil. Trans. A, cci. p. 497 (1903).

§ 'The Emission of Electricity from Hot Bodies.'—O. W. Richardson, 2nd edition (1921).

dynamical considerations that the emission law should be of the form

$$I = AT^2 \epsilon^{-\frac{\phi_0}{kT}}, \quad \dots \quad (3)$$

where A and ϕ_0 are independent of temperature.

Next he tried * to establish the relation (3) on a more solid theoretical basis by applying the quantum theory to the electron gas on the lines suggested and worked out by Keesom †. The theoretical value he obtained for A is

$$\frac{2 \cdot (2\pi)^{\frac{1}{2}}}{9} \cdot \left(\frac{3e}{5}\right)^{\frac{3}{2}} \cdot \frac{MK^2}{Nh^2} \epsilon \times 473,$$

which on numerical computation gives the value 1.5×10^{10} , a value uniformly smaller than that calculated from experimental data by a factor near about $\frac{1}{10}$.

F. V. Hauer ‡ arrived at a slightly modified law from a more phenomenological point of view. With Herzfeld § he

set Planck's expression $\frac{1}{2} \cdot \frac{h\nu}{\epsilon^{kT} - 1}$ for the kinetic energy E

of the electrons (the fraction $\frac{1}{2}$ had been introduced on the supposition that the energy of the electrons is wholly kinetic), and then deduced on considerations of the dissociation equilibrium of ions, electrons, and atoms that the electron concentration inside the metal should not be constant but proportional to $E^{\frac{1}{2}}$, i. e. $n = n_0 E^{\frac{1}{2}}$, which at high temperature may be taken equal to $n_1 T^{\frac{1}{2}}$, where n_1 is a constant. This view has also been taken by J. J. Thomson in his theory of metallic conduction. On putting $n = n_1 T^{\frac{1}{2}}$ in equation (1), the emission law takes the form

$$I = A_2 T \epsilon^{-\frac{\phi}{kT}}. \quad \dots \quad (4)$$

W. Wilson ||, on the other hand, has calculated the emission law on the assumption that all the radiant energy absorbed by hot bodies is converted by quanta into the kinetic energy of the electrons released from the metals. He got a relation practically of the form

$$I = A_3 T^{\frac{1}{2}} \epsilon^{-\frac{\phi}{kT}}. \quad \dots \quad (5)$$

* Phil. Mag. xxviii. p. 633 (1914).

† Comm. Phys. Lab. Leiden, Supp. No. 30 to Nos. 133-144 (1913).

‡ Ann. d. Phys. li. p. 189 (1916).

§ Ann. d. Phys. xli. p. 27 (1913).

|| Ann. d. Phys. xlii. p. 1154 (1913); Royal Soc. Proc. A, xciii. p. 359 (1917).

All these formulæ with $\lambda = \frac{1}{2}, 1, \text{ or } 2$ have been found to represent well the observations on thermionic currents within the range of temperatures 1000° A to 2000° A , provided the constants A and ϕ be regarded as arbitrary.

Very recently Saul Dushman* has worked out an expression for electron emission from metals as a function of temperature in the form

$$I = AT^2 e^{-\frac{L_0}{kT}}.$$

Here A is an absolute constant for all metals, and L_0 is the latent heat of evaporation of electrons at the absolute zero. The basis of his deduction is that the thermal emission of electrons from hot bodies is identical with the process of evaporation from solids or liquids. On this basis, using Nernst's heat theorem and assuming that the electrons outside the hot body behave like an ideal monatomic gas while those inside have no share in the specific heat of the body, he shows that

$$A = \frac{2\pi m e k^3}{h^3}.$$

The first assumptions have been used with success by J. Eggert† and Dr. Megh Nad Saha‡ to calculate the degree of ionization at extremely high temperatures existing in fixed stars and the solar chromosphere. The known values of specific heats of solids also point to the correctness of the last assumption—namely, that the electrons inside a solid have no share in the specific heat of the body. But if the electrons are entirely precluded from their share in the heat motions in the solid state, it becomes difficult to explain the correctness of Wiedemann and Franz's law on the electron theory of conduction.

A better understanding can, however, be reached by the substitution of Planck's quantum expression for the energy content of the electrons inside a solid. With this substitution supplemented by the further hypothesis that the electrons emitted under thermal impulse are identical with the photo-electrons, one can easily arrive at an expression for the thermal emission in the form given by Dushman.

Theory.—We may start by supposing with Born and Kármán that the electrons inside a metal form space-lattices

* Phys. Rev. June 1923.

† Phys. Zeits. Dec. 1919.

‡ Phil. Mag. xl. Oct. 1920.

just as atoms do in a crystal. Then conduction is explained simply by supposing that these electron space-lattices move practically as a rigid structure relatively to the atomic lattice. In the heat motion the electron lattices naturally take part; but the electronic vibrations on account of the smallness of electronic mass possess very high frequency, and hence these vibrations of the electrons, according to Planck's expression for energy, make no appreciable contribution to the atomic heat.

Let us now suppose that the thermal emission of electrons from metals is thermodynamically equivalent to a process of sublimation from the solid to the gaseous state. Now, classical thermodynamics give for the pressure of the vapour as a function of temperature the following equation:

$$\log_e p = -\frac{I_0}{RT} + \int_0^T \left[\frac{\int_0^T (C_p - C_f) dT}{T^2} \right] dT + C, \quad (i.)$$

where I_0 = latent heat of vaporization per gram-atom at the absolute zero;

C_p = sp. heat per gram-atom at constant pressure of the vapour;

C_f = sp. heat per gram-atom of the solid;

C = chemical constant of the substance, which is thermodynamically indeterminate.

If the external electrons possess Maxwell's distribution of velocities, then $C_p = \frac{5}{2} R$. Hence equation (i.) can be written as

$$\log_e p = -\frac{I_0}{RT} + \frac{5}{2} \log T - \frac{1}{R} \int_0^T \frac{E_f dT}{T^2} + C, \quad (ii.)$$

where E_f is the energy of the condensed solid per gram-atom at $T^\circ A$.

Now, supposing the electrons inside the metal to form ideal Born-Kármán crystals, we can use the following quantum theoretical value for their energy content:

$$E_f = \sum_{i=1}^{i=3N} \frac{h\nu_i}{e^{KT} - 1}, \quad \dots \dots \dots (iii.)$$

where the $3N$ quantities, ν_1, ν_2, ν_{3N} form the elastic spectrum of the electronic vibrations.

Now

$$J = \int_0^T \frac{h\nu}{e^{K\nu} - 1} \cdot \frac{dT}{T^2} = - \int_{\infty}^T \frac{dx}{e^x - 1} \left[x = \frac{h\nu}{KT} \right]$$

$$= \left| \log \cdot \frac{e^x}{e^x - 1} \right|_{\infty}^T.$$

But

$$\lim_{x \rightarrow \infty} \log \frac{e^x}{e^x - 1} = 0;$$

$$\therefore J = \log \frac{e^{\frac{h\nu}{KT}}}{e^{\frac{h\nu}{KT}} - 1}. \quad \dots \quad (\text{iv.})$$

Here the frequencies of the electrons stand in no known relation to atomic frequencies. But if we identify the thermally-emitted electrons with the photo-electrons, it is clear that the frequency cannot be less than the threshold frequency of the photoelectric effect, which is for various metals of the order 10^{14} to 10^{15} ; hence it is easily verified that within a range of temperatures 0 to 10^4 °A, $h\nu$ is large compared with KT .

So neglecting 1 compared with $e^{\frac{h\nu}{KT}}$ in (iv.), we have

$$J = \log \frac{e^{\frac{h\nu}{KT}}}{e^{\frac{h\nu}{KT}}} = 0$$

within the specified range of temperatures. Again, since we are here concerned only with the frequencies of those electrons which are emitted, and since for these $\nu_1, \nu_2 \dots \nu_{3N}$ must all be greater or equal to the threshold frequency, we must have

$$\sum_{i=1}^{i=3N} J_i = 0.$$

The equation (ii.) therefore takes the form

$$\log_e p = - \frac{L_0}{RT} + \frac{5}{2} \log T + C. \quad \dots \quad (\text{v.})$$

Now, according to Einstein, the kinetic energy of a

photo-electron ejected from a substance by light of frequency ν is equal to $h\nu$ less the loss of energy in getting out of the substance. The relation may be written as

$$h\nu = \phi + \frac{1}{2}mv^2, \quad (vi.)$$

where $\nu \geq$ threshold frequency,

$\frac{1}{2}mv^2$ = kinetic energy of the ejected electron,

ϕ = work done in tearing the electron away from the atom and in projecting it from the point at which it is torn from the atom up to the point at which it leaves the surface of the body. ϕ , in fact, corresponds to L when expressed in the same units. Since the external electrons are supposed to possess Maxwell's distribution of velocities, it is evident that at the absolute zero the electrons would escape with zero kinetic energy, and hence Einstein's relation (vi.) gives at the absolute zero

$$h\nu_0 = \phi_0 = \frac{L_0}{N},$$

where ν_0 is the threshold frequency.

The equation (v.) therefore reduces to the form

$$\log_e p = -\frac{h\nu_0}{KT} + \frac{5}{2} \log T + C.$$

Now, using the Sackur-Tetrode expression for the chemical constant of a monatomic gas, i. e.,

$$C = \frac{(2\pi m)^{3/2} \cdot K^{5/2}}{h^3},$$

we obtain

$$p = \frac{2\pi m^{3/2} K^{5/2} T^{5/2}}{h^3} e^{-\frac{h\nu_0}{KT}} \quad (vii.)$$

The number of electrons in temperature equilibrium is $n = \frac{p}{KT}$. But, as Richardson has shown, in thermionic currents we do not measure the number of electrons in equilibrium with the hot body, but the number emitted per unit area per sec. which, by the use of the kinetic theory of gases, is given by

$$N = n \cdot \left(\frac{KT}{2\pi m} \right)^{1/2} = \frac{p}{(2\pi m KT)^{1/2}}.$$

Hence we finally arrive at the expression for the thermionic current per sec. per unit area in the form

$$I = Ne = \frac{2\pi me k^3}{h^3} \cdot T^2 \cdot e^{-\frac{h\nu_0}{KT}} \dots \dots \dots \text{(viii.)}$$

Comparison with Experiment.—The expression (viii.) can be written in the form

$$I = AT^2 e^{-\frac{b_0}{T}}.$$

Using the values,

$$K = 1.372 \times 10^{-16} \text{ erg/degree,}$$

$$h = 6.55 \times 10^{-27} \text{ erg/sec.,}$$

$$e = 1.59 \times 10^{-19} \text{ e. s. u.,}$$

$$m = 8.995 \times 10^{-28} \text{ gram.}$$

The universal constant

$$A = 1.80 \times 10^{11} \text{ e. s. u./cm.}^2 \text{ deg.}^2$$

$$= 60.2/\text{cm.}^2 \text{ deg.}^2$$

The constant $b_0 = \frac{h\nu_0}{K}$ may be regarded as a sort of characteristic temperature of the electrons inside the solid.

The value of b_0 has been computed from the thermionic current data of the various observers, using the expression for emission per unit area per sec. in the form

$$I = 60.2 T^2 e^{-\frac{b_0}{T}}.$$

The intrinsic potentials ϕ_0 of various metals calculated both from thermionic and photoelectric data are given in the following table for comparison :—

$$\phi_0 = \frac{Kb_0}{e} = .862 \times 10^{-4} b_0 \text{ volt [Thermionic].}$$

$$\phi = \frac{h\nu_0}{e} = \frac{hc}{e\lambda_0} = \frac{12.36 \times 10^{-5}}{\lambda_0} \text{ volt [Photoelectric].}$$

λ_0 is the wave-length corresponding to Photoelectric threshold.

Metals.	$b_0 \times 10^{-4}$.	$\phi_0 = \frac{K h_0}{e}$ volts.	$*\lambda_0 \times 10^5$ cms.	$*\phi_0 = \frac{C h}{e \lambda_0}$ volts.	Resonance potential of metallic vapours.
¹ Pt.....	4.925	4.25	2.80	4.42	...
² W.....	5.260	4.53	2.20	5.70	...
³ C	5.267	4.54	2.60	4.75	...
⁴ Na	2.498	2.15	5.46	2.26	2.12
⁵ Cs.....	1.600	1.38	8.25	1.49	1.48
⁶ Ca	3.320	2.86	3.70	3.34	2.85
⁷ CaO	4.043	3.48	...	...	...
⁸ MgO	3.795	3.26	3.50	3.53	2.65 } 4.42 }

* Hughes's Report on Photoelectricity (Bulletin of the National Research Council, No. 10, April 1920).

¹ Schlichter, *Ann. der Phys.* xlvii. p. 129 (1908).

² Langmuir, *Phys. Zeits.* Jahrg. 15, p. 525 (1914).

³ Deiningcr, *Ann. der Phys.* xxv. p. 285 (1908).

⁴ Richardson, *Phil. Trans. A.* cci. p. 497 (1903).

⁵ Langmuir, *Science Abstracts, A*, 1436 (August 1923).

⁶ Horton, *Phil. Trans. A.* ccvii. p. 149 (1907).

⁷ Deiningcr, *Ann. der Phys.* xxv. p. 285 (1908).

⁸ Yentzsch, *Ann. der Phys.* xxvii. p. 129 (1908).

Discussion.—A glance at the table shows favourable agreement of the theory with the results of various observers on thermionic current. Unfortunately, as Hughes has pointed out in his Report on Photoelectricity, “the variations in the values for the thermionic results are only equalled by the uncertainty in the Photoelectric threshold.” Yet the order of correspondence between the values of ϕ_0 calculated from thermionic data and also from photoelectric threshold certainly justifies the assumptions involved in the deduction of the thermionic emission law.

The actual mechanism by which electrons obtain their energy for emission is, up till now, not clear. The explanation of photoelectric effect on Einstein's theory, while leading to results in good agreement with experiment, is silent about the actual processes involved.

Photoelectrons have been up till now regarded as loosely bound with the atoms, while thermally-emitted electrons

have been identified with the so-called "free electrons." To my mind, it seems that the photoelectrons and the electrons emitted by heat must be identical in nature in whatever way they may exist in the metals relative to the atomic nuclei. It seems quite possible, as Wilson contends, that the actual mechanism of the thermal emission is really a kind of auto-photoelectric resonance of the electrons caused by the light-radiation supplied by the hot body itself. A comparison of the resonance potentials of the alkalis and the alkaline earth vapours with the intrinsic potential ϕ_0 is very suggestive in this direction, and leads one to believe that the liberating rôle is played by a resonance process. Further speculation on this point must be deferred for the present, for the data available are not sufficient to formulate a definite theory on the subject.

In conclusion, I wish to record my best thanks to Prof. C. V. Raman and Dr. P. N. Ghosh for their helpful guidance in writing this paper.

Oct. 10, 1923.

XLIX. *The Electronic Theory of Valency.*

By B. FLÜRSCHHEIM, *Ph.D.**

A RECENT issue of this Magazine † contains a paper by Prof. Lowry, written for a discussion on Valency held by the Faraday Society last July, and largely devoted to a criticism of conceptions advanced by the present writer. It may therefore be desirable to present the reply which has been contributed to the said discussion.

Nearly all the authors of electronic valency theories have concentrated on the "alternating effect" caused by substituents in aromatic rings. Reviewing briefly the theoretical aspect of aromatic substitution, we shall see whether "the introduction of an additional mechanism," in this case electronic bonds, has brought closer agreement between theory and facts.

The hypothesis that a substituent may cause the distribution of chemical force to alternate over a whole chain of atoms was first advanced in 1902 ‡ and developed between

* Communicated by the Faraday Society.

† *Phil. Mag.* Nov. 1923, p. 1013.

‡ Flürscheim, *Journ. f. prakt. Chem.* lxvi. p. 16 (1902).

1905 and 1910 *. The essential idea, partly based on Claus' and Werner's general conception of the variability of the affinity content in bonds, was this: if an atom, such as tervalent nitrogen, with more available residual affinity than hydrogen, is linked, for instance, to a carbon atom in benzene, it makes a greater demand than would hydrogen on the affinity force of this carbon atom. The equilibrium of forces which existed in benzene is thereby disturbed, because carbon 1 has now less affinity left to bind carbons 2. These now have more unbound affinity available than they had in unsubstituted benzene, and since there must be an equilibrium between free and bound forces, the free affinity at carbons 2 and the bound affinity between carbons 2 and 3 become greater than in benzene, and so on. It is therefore to carbons 2 and 4 that a reacting molecule is attracted, forming first an intermediate (Kekulé) molecular addition product, which then changes to a substitution derivative with the new substituent in 2 or 4. If an atom, such as pentavalent nitrogen, disposes of less available residual affinity than hydrogen, the reverse process occurs, with substitution in 3.

It has also been shown that the above simple principle leaves no loophole for an arbitrary interpretation of the relative directing effect of different substituents, and a careful record of the numerous facts published so far has not revealed a single proved case in disagreement with this generalization. The writer had refrained from basing it on any assumptions concerning the ultimate nature of chemical affinity itself. Of late, however, others, while adhering to this alternating principle, have stated a special case by introducing the supposed electrical nature of chemical affinity. "Affinity demand" has become an "electron demand." The result would be a narrower interpretation, but—though by no means the only possible—deeper foundation, provided that agreement with chemical experimental data remained unaffected and that the physical assumptions were sound. Let us see whether this is the case, and first tabulate the essential postulates of the various substitution theories, in chronological order.

Non-electronic :—

Flürscheim: varying alternation through varying affinity demand of substituting atom (named "key atom" by Lapworth); molecular addition at maximum free affinities.

* *Ibidem*, lxxi. p. 497 (1905); lxxvi. pp. 165, 185 (1907); Journ. Chem. Soc. xc. p. 718 (1909); xcvi. p. 84 (1910); *Ber. d. deutsch. chem. Ges.* xxxix. p. 2015 (1906).

Electronic :—

Fry, Vorländer : $\pm$ alternating principle.

Lapworth, Robinson : *o-p* : conjugated addition ; *m* : $\pm$ alternation.

Pauly : identical with Flürscheim, excepting that key atom with affinity demand $>H$ is defined as strongly negative atom attracting an electron.

Eastman : negativity of substituent and its size probably determine orientation.

Huggins : *o-p* : no conjugation with ring ; *m* : electronic conjugation with ring.

Crocker : substituting atom with electron affinity causes removal of electrons from *o*-, *p*-, and thereby *o-p*-substitution, and *vice versa*.

Lowry : $\pm$ alternation ; avoidance of crossed polarities, because less stable ; similarly polarized groups occupy metapositions ; addition at side chain or in 1:2 and 1:4 in ring may precede substitution.

A list of well over 100 facts, to be published soon, proves conclusively :

1. That there is no definite $\pm$ alternation in chains, since regarding substitution of hydrogen and replacement of substituents in aromatic rings, stability of crossed polarities, and the effect of substituents on the affinity constants of organic acids, facts are often diametrically opposed to the requirements of $\pm$ alternation ;

2. That substitution of hydrogen in the benzene ring is not preceded by 1:2- or conjugated addition, but by molecular addition at a single atom ;

3. That there is no regular connexion between the electro-polar nature of an atom and its directing effect ;

4. That the "negativity" and size of a whole group do not determine whether it will direct to *o-p*-, or to *m*-.

In other words, not one of the above assumptions in any of the above electronic theories can bear a thorough comparison with experimental evidence. This refers, of course, to these theories as they appear to present themselves at present. In their paper before the Faraday Society, Professors Lapworth and Robinson promised further developments as to the interpretation of their theory, which will be awaited with general interest.

The physical assumptions underlying the electronic bond theories, though not so easily refutable experimentally, nevertheless appear to offer considerable logical difficulties.

To mention a few :

1. It has not been possible, so far, to devise even a hydrogen molecule model, with electron bonds, without conflicting with physical postulates.

2. Professor Lewis * has shown, using chloro-acetic acid as an example, that the electron demand of chlorine must cause a shifting of electrons toward the chlorine, therefore in *one* direction, throughout the chain. "General polarity" in Michael's sense would thereby be satisfactorily explained, including the gradual lessening of the effect with an increase in the number of intervening atoms †. Positive-negative alternation, however, pre-supposes a shifting of electrons in *opposed* directions. Since the general polar effect is admittedly always present, electrons must be shifted, simultaneously and in the same molecule, in the same and in opposed directions !

3. The idea that an atom in which an electron has been moved outward tends to slacken its hold on some of its remaining electrons is, of course, contrary to the requirements of electrostatics. It is explained by an "octet stability" assumed *ad hoc*. Since organic molecules contain atoms with substantially differing volumes and total numbers of electrons, it requires courage to assume that they all share the preference shown by many authors for the number 8 ; and that, to gratify this preference, they will set aside the fundamental law of electrostatics.

Without electronic bonds, the author has shown that it is possible to co-ordinate, not only the numerous observations on aromatic substitution, but many others, such as the thermic dissociation of quaternary compounds, equilibria in pseudo-acids and pseudo-bases, the affinity constants of organic acids and bases. His efforts in this latter direction form the subject of an interesting analysis by Professor Lowry. To reply intelligibly, the principles on which the author's co-ordination of affinity constants was based must be briefly explained.

* Journ. Amer. Chem. Soc. xxxviii. p. 762 (1916).

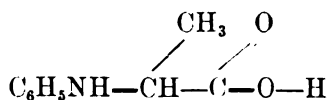
† This interpretation, embodied in an advance reprint of this contribution, has since been utilized by Lapworth and Robinson, in a letter to 'Nature' (Nov. 17th, 1923). The present author disagrees, however, with certain conclusions in this letter, which appear to be based on an erroneous interpretation of Sir J. J. Thomson's deductions in the September issue of this Magazine.

Chemical reactions are, in the general case, governed by three internal factors:—

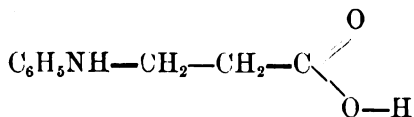
1. The *amount* of affinity available at the reacting atom (quantitative factor), which depends on the distribution of affinity force in the molecule.
2. The *kind* of affinity available at the reacting atom (polar factor = general polarity).
3. The magnitude of steric hindrance affecting the reacting atom (steric factor).

It has been shown that the relative order in which different substituents in varying positions affect each factor can be ascertained by independent evidence. There are obviously cases where one or two of these factors are practically eliminated. In the replacement of hydrogen in a mono-substituted benzene-derivative, for instance, the steric factor at the meta- and para-atoms is the same, and the polar factor differs only slightly, so that in this simplest case it was possible to predict the place of substitution (*o-p-* as against *m-*) by the quantitative factor alone, the other factors merely affecting the relative proportions of the *o-* compared with the *p-* compound.

Taking, now, an organic acid, such as propionic, and a substituent with a greater affinity demand than hydrogen, such as $\text{—NH} \cdot (\text{C}_6\text{H}_5)$, we have:



and



wherein thick lines denote an increased amount of bound affinity, compared with the corresponding bond in unsubstituted propionic acid, whereas thin lines denote the reverse. In the β -acid the ionizable hydrogen is therefore more strongly held than in propionic acid, and will dissociate less easily. The reverse holds for the α -acid.

The polar factor of the substituent affects the affinity of the carboxyl-oxygen for the electric charge, a “negative” substituent increasing it, and *vice versa*. Professor Lowry

maintains that the anilino-group is "negative," others may hold a contrary opinion; this question is immaterial to the present argument, since the general polar effect must be in the same direction, whatever the position of the substituent, and therefore cannot account for the fact that the α -anilino-acid is stronger, and the β -acid weaker, than propionic.

The steric factor always increases the strength of an acid, since in the electrolytic equilibrium

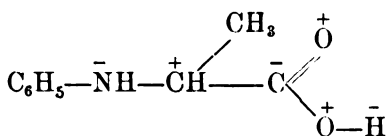


the unimolecular reaction from left to right is not affected by steric hindrance, whereas the bimolecular reaction from right to left is retarded thereby (solvation rendering the hydrogen ion large enough to be thus affected). Neither can the steric factor therefore account for the above inversion in β - compared with α -. This inversion would, as has just been shown, result from the quantitative factor by itself; and since trivalent nitrogen, as evidenced by its directing power in the benzene nucleus, has the greatest affinity demand, and the quantitative effect is therefore at its maximum, the resultant of all three factors also causes inversion.

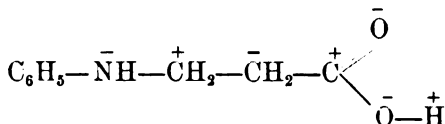
Professor Lowry suggests that the low constant of the β -acid might be explained by assigning to it the constitution of an inner salt. But this is excluded. An anilino-group is incapable of forming an inner salt with a carboxyl-group. In *o*-aminobenzoic acid the dissociation constant of the amino-group is only 15 per cent. less than in the corresponding methyl-ester; in *m*-aminobenzoic acid, though its configuration is unfavourable to inner salt formation, this difference is actually greater and in the same direction. In the anilino-aliphatic acids, on the other hand, the excess of strength of the α -acid over that of the β -acid is of an entirely different order, reaching for iso-butyric acid well over 1000 per cent. Moreover, inner salts invariably melt at very high temperatures, generally with decomposition, and are more soluble in water than in organic solvents. For instance, both α - and β -aminopropionic acids—which both form inner salts on account of their unsubstituted (by phenyl) and therefore very much more basic amino-group—do not melt at all and are very easily soluble in cold water. But β -anilinopropionic acid melts at 59° to 60° (even lower than its α -isomeride (m.p. 162°) to which Professor Lowry does not assign an inner salt constitution), and is little

soluble in cold water, but easily in organic solvents. All these facts serve equally to disprove assumptions, similar to those of Professor Lowry, made by Vorländer* and by Adams† (to which Professor Lowry has kindly called the writer's attention).

While thus affording a striking confirmation of the above non-electronic theory, the anilino-acids—amongst others—furnish a disastrous test for electronic theories. There we have, for instance :—



and



In other words, the acid which experience proves to be weaker than propionic acid should, in electronic parlance, possess carboxyl-oxygen with a particular avidity for electrons, and *vice versa*. And this, too, where we deal, for once, not with assumed, unproved electrons, but with a real, demonstrable electric charge.

In the other series of constants discussed by Professor Lowry, most of the values differ relatively little, and in no case is there a substituent with such an outstanding quantitative effect as that of tervalent nitrogen. In such cases the application of all three factors cannot leave the quantitative effect in such a predominant position, as a glance at the author's papers of 1909 and 1910 will show, where all three factors have been applied to numerous constants (including the anilino-acids), by a concordant method throughout which automatically excludes arbitrary adjustments. Professor Lowry proves that the application of the quantitative factor alone does not yield general agreement—a fact not only in conformity with the author's theory, but postulated by it.

* *Lieb, Annalen*, cccxx. p. 99 (1902).

† Journ. Amer. Chem. Soc. xxxviii. p. 1508 (1916)

It can be shown that when all three factors are applied, all the constants examined by Professor Lowry are in agreement with the theory, subject to the following remarks:

1. For vinylacetic acid, Fichter's value (3.8×10^{-5}) should be replaced by Zelinsky's re-determination (4.65×10^{-5}).

2. As to unsaturated acids, in general, one must agree with Professor Lowry that there is uncertainty where only one of the two *cis-trans*-isomerides is known. But it can be shown that this affects only $\alpha\beta$ -unsaturated acids.

3. That according to the author's theory *n*-valeric acid must not be stronger than *n*-butyric acid, is also a point on which Professor Lowry is quite correct. All the published comparative determinations for these two acids have therefore been examined. There are three from Ostwald's laboratory:

	N-Butyric.	N-Valeric.	Date.
1	1.49×10^{-5}	1.61×10^{-5}	1889
2	1.52×10^{-5}	1.50×10^{-5}	1895
3	1.75×10^{-5}	1.56×10^{-5}	1905

In addition, there are constants by Billitzer:

4	1.54×10^{-5}	1.61×10^{-5}	1899
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The discrepancies are therefore considerable, but only in No. 2 (Francke) have *both* acids been carefully purified. There is, at any rate, no reason to conclude that *n*-valeric is stronger than *n*-butyric acid. But butyric, in spite of the positive effect of methyl, should be and is somewhat stronger than propionic acid (steric effect of β -substituent, see 1909 paper, p. 729).

To summarize: organic facts can be concordantly co-ordinated on the basis of varying affinity demand in conjunction with general polarity and steric hindrance. Electronic bonds, however, are confronted with serious difficulties by the facts of organic chemistry as well as by the postulates of physics.

Fleet, Hampshire.

*L. A New Form of Electrometer.**By F. A. & A. F. LINDEMANN and T. C. KEELEY*.*

[Plate II.]

AS was shown in a paper published some years ago† numerous problems in astrophysics could be solved if a convenient photoelectric method were developed for measuring the amount of light received from stars, nebulae, comets, etc. For this purpose the photoelectric cell is best fixed just behind the focus of an equatorial telescope and the current produced by the light which falls upon the cell is measured by means of an electrometer. In order to keep the electrostatic capacity of the system as small and constant as possible, it is desirable to fix the electrometer and the cell rigidly together. This also facilitates drying and thus diminishes any leakage. This arrangement involves considerable difficulties, however, since no existing form of electrometer maintains a constant sensitivity, and still less a steady zero, when moved about at the end of an equatorial telescope. The object of this paper is to describe a new form of electrometer which is free from these defects. Since it is capable of a sensitivity as great as that of any existing electrometer, although its period is less than one second and its capacity less than 2 cm., it may be useful for many laboratory purposes even where independence of the zero and sensitivity to tilt is not essential.

The principle of this electrometer is the same as that of the quadrant electrometer; it consists essentially of a needle, which in this case really has the shape of a needle, suspended at its centre on a torsion fibre in such a way that it can rotate between four cross-connected plates which take the place of the ordinary quadrants. The important innovation is that the torsion fibre is fixed at both ends under tension so that the centre of rotation of the needle is fixed, and its rotation can therefore be determined by observing the motion of one end through a microscope. This renders a mirror unnecessary, and, consequently, the moment of inertia of the moving parts can be reduced to a minimum. Hence a very small torsional restoring force may be used without increasing the period unduly.

The most suitable dimensions can be found by considering

* Communicated by the Authors.

† Monthly Notices R. A. S. lxxix. 5. p. 343 (1919).

the sensitivity in terms of the dimensions of the various parts. If r_1 is the radius of the torsion fibre, l_1 its semi-length, and n_1 the torsion modulus, the restoring couple for unit angular displacement is $\Gamma_0 = \frac{\pi n_1 r_1^4}{l_1}$. If r_2 is the effective radius of the needle, l_2 its semi-length, and ρ_2 its density, the moment of inertia I is $\frac{2}{3}\pi\rho_2 r_2^2 l_2^3$. Hence the free period *in vacuo* will be

$$T_0 = 2\pi\sqrt{\frac{I}{\Gamma_0}} = 2\pi\sqrt{\frac{2\rho_2 r_2^2 l_2^3 l_1}{3n_1 r_1^4}} \dots \dots (1)$$

If an earthed conductor of capacity C in an electric field F be moved a distance δ in the direction of the field a charge $C\delta.F$ will be induced upon it, assuming its reaction on the field to be negligible. Hence if c_2 be the capacity of the needle per unit length, rotation through an angle θ will induce a charge $\theta l_2 c_2 F dl$ in each element dl . The electric field therefore tends to make the needle unstable, the couple

to which it gives rise being $2F \int_0^{l_2} \theta l_2 c_2 F dl$, which reduces for unit angular displacement to $\frac{2}{3}c_2 F^2 l_2^3$. Hence the effective restoring couple Γ will be Γ_0 diminished by this electric couple, *i. e.* $\Gamma = \frac{\pi n_1 r_1^4}{l_1} - \frac{2}{3}c_2 l_2^3 F^2$. The period in the field therefore, if damping be neglected, will be

$$T_1 = 2\pi \sqrt{\frac{\frac{2\rho_2 r_2^2 l_2^3}{3}}{3\left(\frac{\pi n_1 r_1^4}{l_1} - \frac{2}{3}c_2 l_2^3 F^2\right)}} = 2\pi \sqrt{\frac{2\rho_2 r_2^2 l_2^3 l_1}{3\pi n_1 r_1^4 - 2c_2 l_2^3 F^2 l_1}} \dots \dots (2)$$

If a charge at potential v is communicated to the needle, each element dl will contain a quantity of electricity $vc_2 dl$. The turning moment in a field F will therefore be

$$2 \int_0^{l_2} v F c_2 l dl = v F c_2 l_2^2,$$

taking account of both arms of the needle. Hence the needle will turn through an angle $\theta = \frac{v F c_2 l_2^2}{\Gamma}$ and its end will be displaced by a charge at unit potential through a distance

$$\frac{\theta l_2}{v} = \frac{3 F c_2 l_2^3 l_1}{3\pi n_1 r_1^4 - 2c_2 l_2^3 F^2 l_1} = \frac{3 F c_2}{8\pi^2 \rho_2 r_2^2} \cdot T_1^2 \dots \dots (3)$$

This quantity may be regarded as a measure of the sensitivity of the instrument. The number of divisions per volt depends simply upon the magnification which can be obtained with the microscope used.

At first sight it might appear that one could increase the sensitivity for a given period almost indefinitely by increasing the field F and diminishing the effective radius of the needle r_2 .

This is not true, however, because a lower limit to r_2 is imposed by various considerations. For the purpose for which the electrometer was originally designed it was necessary that its zero and sensitivity should not be materially altered when the equatorial to whose end it was fixed was directed at different celestial objects. Hence it was important that the needle should not bend appreciably under its own weight. If the maximum displacement of the end when the electrometer is rotated which one decides to admit

is called δ_2 this fixes a lower limit to $r_2 = l_2^2 \sqrt{\frac{\rho_2 g}{2E\delta_2}}$, E being, of course, Young's modulus.

Even if one is content to use the electrometer in one position and thus is able to neglect the effect of gravity, it is not possible to reduce r_2 indefinitely. All the above calculations are made on the assumption of a rigid needle. If the needle is too thin it will bend under the electric force acting on its own induced charge. It is obviously essential that the needle should not become unstable under these conditions, and it is undesirable that this electrostatic bending should be comparable to the torsional deflexion. The amount of bending which occurs under the electric force is somewhat complicated to calculate accurately, since the charge generated is proportional to the displacement. The order of magnitude of the quantities involved may be estimated, however, by considering that half the capacity of the needle is effective, and that this, with the corresponding charge, is placed at the end of the needle. In this case the charge induced by the bending of the end through a distance δ is $\frac{1}{2}l_2 c_2 F \delta$, and the force which comes into play is $\frac{1}{2}l_2 c_2 \delta F^2$. As the restoring force is $\frac{3\pi r_2^4 E \delta}{4l_2^3}$ the needle becomes unstable if

$$\frac{1}{2}l_2 c_2 F^2 > \frac{3\pi r_2^4 E}{4l_2^3}.$$

In practice the limit of r_2 which was used was that set by

the gravitational bending. Taking the permitted shift of the zero when the electrometer is reversed as 10^{-3} cm. this leads to a value of r_2 large enough to be stable for fields up to 10 E.S.U., *i. e.* 3000 volts per cm., and fields greater than this are not usually convenient to use.

If one inserts the above value for r_2 in the equation for the sensitivity $\frac{\theta l_2}{v} = \frac{3Fc_2}{8\pi^2\rho_2r_2^2} \cdot T_1^2$, one finds

$$\frac{\theta l_2}{v} = \frac{3T_1^2}{8\pi\rho_2l_2^2} \sqrt{\frac{3\pi}{2}} \cdot EF^2c_2^3.$$

It is evident from this that the sensitivity may be increased by reducing l_2 , but here again one cannot proceed to extremes.

A limit is set by the technical difficulty of constructing an instrument on a very small scale. The quadrants, or rather plates, cannot be too close together, as the needle must be mounted between them. But the plates acting upon the other end of the needle must be at such a distance from the first pair that their field is not disturbed unduly. Hence the pairs of plates must be at a distance from one another great compared to the distance between the two plates in a pair, and this makes it impossible to use a very short needle, *i. e.* reduce l_2 indefinitely.

As a matter of fact, the optimum conditions according to this formula are not of great practical importance, since air-damping, which has been treated as negligible above, becomes extremely important when the restoring force is very much reduced. It is true that the suspension can be enclosed in an air-tight box and the air removed, but the considerable increase in sensitivity so attained rarely makes up for the inconvenience this method involves. For most purposes it is preferable to avoid a vacuum, even at the expense of sensitivity, and to choose the dimensions of fibre and needle with a view to obtaining the best conditions of sensitivity and period in air at ordinary pressure.

If the damping per unit length is μr_2 the damping couple on the needle will be $2 \int_0^{l_2} \mu r_2 l \cdot l \dot{\theta} dl = \frac{2}{3} \mu r_2 l_2^3 \dot{\theta} = \kappa \dot{\theta}$. The equation of motion therefore becomes $\ddot{\theta} + \frac{\kappa}{I} \cdot \dot{\theta} + \frac{\Gamma}{I} = 0$, which reduces, in the case of heavy damping, to $\theta = \theta_0 e^{-\frac{\Gamma}{\kappa} \cdot t}$.

If t_0 represents the time in which the deviation from the final position is reduced from θ_0 to $\frac{\theta_0}{e}$, then

$$t_0 = \frac{\kappa}{\Gamma} = \frac{2\mu r_2 l_2^3 l_1}{3\pi n_1 r_1^4 - 2c_2 l_2^3 F^2 l_1}.$$

Hence, from (3)

$$\frac{\theta l_2}{v} = \frac{3F^2 c_2 t_0}{2\mu r_2}.$$

In general F will be increased to a value near the unstable value where $3\pi n_1 r_1^4 = 2c_2 l_2^3 F^2$. If this value is inserted the above expression may be reduced to

$$\frac{\theta l_2}{v} = \sqrt{\frac{9\pi^3 c_2 \rho_2}{\mu^2}} \cdot \frac{t_0}{T_0}.$$

Since $c_2 \left(= \frac{1}{2 \log \frac{l_2}{r_2}} \right)$ scarcely varies and ρ_2 and μ cannot

be altered very much, it is evident that the maximum sensitivity goes up as the period *in vacuo* is diminished. It must be remembered, however, that the field on the plates goes up in the same proportion as shown in the previous formula. It follows that for a given field the maximum sensitivity is reached when the diameter of the needle is a minimum. The diameter of the needle is determined by the condition that it must not bend more than a certain amount.

being roughly given, as shown above, by $r_2^4 = \frac{2}{3} \cdot \frac{c_2 F^2}{\pi E} \cdot l_2^4$. Hence the limiting sensitivity is given by

$$\frac{\theta l_2}{v} = \sqrt{\frac{4}{32} \cdot \frac{243}{32} \cdot F^2 c_2^3 \pi E} \cdot \frac{t_0}{\mu l_2}.$$

As was remarked above, l_2 cannot be reduced inordinately owing to constructional difficulties. Hence the sensitivity can only be increased, without sacrificing rapidity of working, by increasing the field. In principle, of course, this could be made equal to the sparking potential. In practice it is more convenient to work with much lower fields, since, as stated, the distance between the plates must be some 4 to 6 mm., and a large field would therefore entail a very large battery or other source of constant high potential.

The form finally adopted for general use is shown in figs. 1 and 2, Pl. II. In this instrument the silica torsion

fibre A (much exaggerated in the illustration to render it visible) is about 1.4 cm. long and 6μ thick, and is stretched under a tension of about half the breaking strain on a U-shaped frame B. This is made of 3 mm. silica rod with saw-slits about 1 mm. deep at the ends in which the fibre is mounted. As the frame and the fibre are both of silica no change of tension occurs when the temperature changes.

The fibres are silvered by sputtering in the usual way, and one end is fixed in the slit with Wood's metal. A thin copper wire is inserted in the slit at the same time forming the lead. The other end of the torsion fibre is fixed in the other slit with shellac. In order to assure the necessary tension, a weight of appropriate size is attached temporarily to the protruding end and the shellac melted with the frame in a vertical position. When it has re-solidified, the protruding portion is removed.

In order to facilitate balancing, the needle C is composed of two equal parts placed parallel to one another on each side of the torsion fibre. They were usually about 25μ thick and 2 cm. long and made of silvered glass. The ends are sealed together, and the whole attached in the plane of the frame rigidly to the torsion fibre by electrolytically deposited copper.

The quadrants D consist of plates about 1.5 cm. broad and 1 cm. high, in which slots are cut about 2 mm. broad through which the needle can pass. These plates are mounted about 5 mm. apart on 3 mm. silica rods, E. The suspension is mounted between them so that the centre of rotation coincides with the centre of symmetry of the four plates. The whole is enclosed in a small metal box about 4.5 cm. long by 2.8 cm. broad and 3 cm. high, made of a suitable aluminium alloy, in the centre of the top and bottom of which are holes about 10 mm. in diameter closed with microscope coverslides. The leads from the two sets of plates are carried out at one end insulated by silica tubes, the lead from the needle being carried out, similarly insulated, at the other. An earthing terminal on the box enables the effect of stray electrostatic fields to be eliminated.

For use, this box—which only weighs about 80 grammes—is placed on an ordinary microscope stand and the pointer at the upper end of the needle is observed, illumination being obtained in the ordinary way through the hole in the bottom of the box. The connexions can, of course, be made in any of the ways used in ordinary quadrant electrometers. On account of the small restoring force and moment of

FIG. 1.

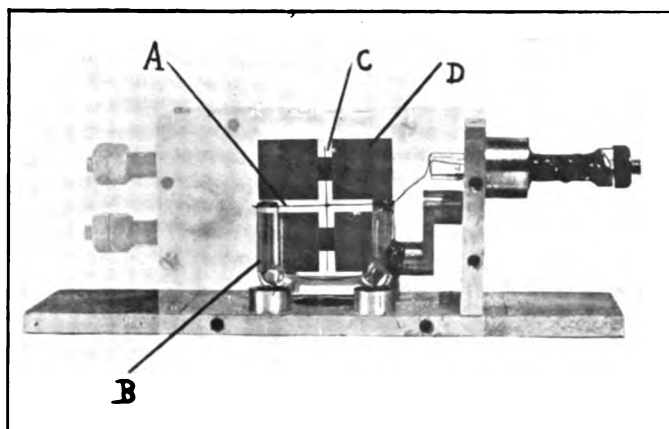
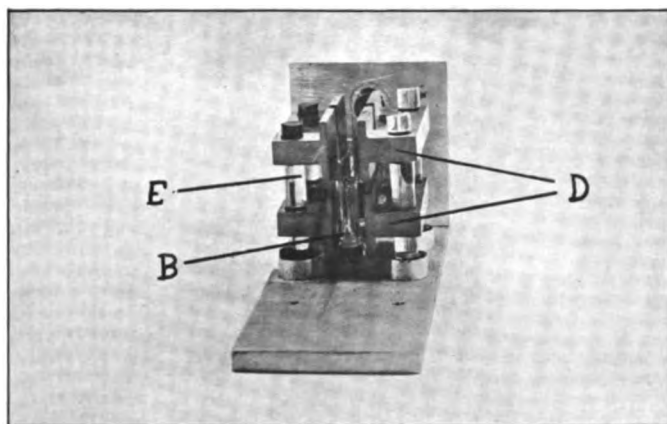


FIG. 2.



inertia, air-damping with the above dimensions is about right to render the instrument practically aperiodic.

For use on an equatorial the microscope was permanently fixed to the lid of the box and artificial light from a small four-volt lamp used. In order to facilitate setting the zero and varying the sensitivity, the plates were further made movable on slides, their positions being adjusted by screws with divided drums, passing through the sides of the box. The whole electrometer was then screwed onto the brass cell box, in which the photoelectric cell was mounted, and this was rigidly attached to the equatorial. For general use, the form described above is, however, probably preferable on account of its simplicity: adjustment of zero and sensitivity can be accomplished by altering the potentials on the plates, fine adjustment by means of a potentiometer in the middle of the high tension batteries being advisable.

The constants of the instrument are in reasonably close agreement with the formulæ developed above. For the sake of completeness the exact constants of one instrument may be given. The torsion fibre is 1.4 cm. long and about $6\ \mu$ thick. The needle consists of two silvered glass fibres 0.9 cm. long and $17\ \mu$ thick. The plates are 0.6 cm. apart, and the instrument becomes unstable at about 100 volts. The capacity is 1.3 cm. and the free period (calculated *in vacuo*) is about 0.15 second. The zero moves about 0.06 mm. on turning the instrument through 90° , 0.00 mm. for 180° , 0.008 mm. for 270° . The sensitivity is completely independent of tilt. With a field of 160 volts/cm., corresponding to a potential of 97 volts, the deflexion reaches $\frac{9}{100}$ of its final value in about one second. The pointer moves 0.76 mm. per volt with this field, so that with a $\frac{1}{4}$ -inch objective and a $\times 20$ eyepiece a sensitivity of 450 divisions per volt can be attained. Under these conditions perfectly satisfactory definition can be obtained and $\frac{1}{10}$ of a division can be read without difficulty. As is evident, no attempt was made to use a very strong field. In most cases one or two sixty-six volt boxes, such as are on sale for wireless sets, sufficed. If desired, one can use a finer torsion fibre and batteries of ten or twelve volts across the plates. With a suitable leak these electrometers, of course, make very convenient quick period galvanometers, sensitive to currents of 10^{-10} to 10^{-14} ampere, and as the sensitivity is almost equal to that of a Dolezalek electrometer with a very much smaller capacity and period, it would seem that it may be useful for many purposes, even where convenience in using is not so much an object as great sensitivity and accuracy.

LI. *Note on Mr. Harward's Paper on the Identical Relations in Einstein's Theory.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper on "The Identical Relations in Einstein's Theory" in the August 1922 number (pp. 380–382) of the *Philosophical Magazine*, Mr. Harward proves a general theorem which he discovered for himself, although he did not believe it to be undiscovered before. The theorem is:

$$(B^{\rho}_{\mu\nu\sigma})_{\tau} + (B^{\rho}_{\mu\sigma\tau})_{\nu} + (B^{\rho}_{\mu\tau\nu})_{\sigma} = 0.$$

It may be of interest to mention that this theorem is known, especially in Germany and Italy, as "Bianchi's Identity," having been published by L. Bianchi in the *Rendiconti Acc. Lincei*, xi. (5) pp. 3–17 (1902). In this paper, Bianchi already deduced from this theorem the identity Mr. Harward refers to:

$$G^{\nu}_{\mu\nu} = \frac{1}{2} \frac{\partial G}{\partial x^{\mu}}.$$

The identity of Bianchi seems, however, to be published for the first time by E. Padova (*Rendiconti Acc. Lincei*, v. (4) pp. 174–178, 1889), who obtained it from G. Ricci. Compare for this the book of Struik (*Grundzüge der mehrdimensionalen Differentialgeometrie*: Berlin, J. Springer, 1922, p. 148), where the theorem is proved in a similar way as Mr. Harward does. A similar proof was already given by Schouten (*Mathem. Zeitschr.* xi. pp. 58–88, 1921).

The theorem can be generalized by taking geometries with a more general parallel displacement than in ordinary Riemann geometry. We then obtain the generalized geometries of Schouten (*Mathem. Zeitschr.* xiii. pp. 56–81, 1922), of which the geometries of Weyl and Eddington (*cf.* Eddington's 'Mathematical Theory of Relativity,' Ch. vii.) are special cases. Schouten, in a recent paper (*Mathem. Zeitschr.* xvii. pp. 111–115, 1923), proved the generalization of Bianchi's Identity for a geometry of which a geometry with a symmetrical displacement (that is, a geometry in which $\Gamma^{\mu}_{\nu\alpha} = \Gamma^{\mu}_{\alpha\nu}$, *cf.* Eddington, *loc. cit.* p. 214) is a special case. This special case is treated by A. Veblen (*Proc. Nat. Ac. of Sciences*, July 1922). R. Bach already gave the generalization for the geometry of Weyl (*Mathem. Zeitschr.* ix. pp. 110–135, 1921).

A simple proof of Bianchi's Identity, which holds for a

geometry with a symmetrical displacement and was suggested to us by Prof. Berwald at Prague, can be given in the following way :—

$$\text{Let} \quad \Gamma_{\nu\alpha}^{\mu} = \Gamma_{\alpha\nu}^{\mu}.$$

We can introduce in this case, in a regular point x_0^{ν} , a system of so-called geodesic coordinates x^{ν} , by the transformation :

$$x^{\nu} - x_0^{\nu} = x^{\nu} - \frac{1}{2} \Gamma_{\lambda\mu}^{\nu} x^{\lambda} x^{\mu}$$

(cf. Weyl, *Raum, Zeit, Materie*, 4th edition, §14, p. 101).

For these coordinates, all $\Gamma_{\nu\alpha}^{\mu}$ vanish in x_0^{ν} , and covariant differentiation in x_0^{ν} becomes identical with ordinary differentiation.

When now we evaluate the expression

$$(R_{\mu\nu\sigma}^{\rho})_{\tau} + (R_{\mu\sigma\tau}^{\rho})_{\nu} + (R_{\mu\tau\nu}^{\rho})_{\sigma} \quad . \quad . \quad . \quad (1)$$

for the generalized Riemann-Christoffel symbols

$$R_{\mu\nu\sigma}^{\rho} = \left(\frac{\partial}{\partial x^{\nu}} \Gamma_{\mu\sigma}^{\rho} - \frac{\partial}{\partial x^{\sigma}} \Gamma_{\mu\nu}^{\rho} \right) + \left(\Gamma_{\kappa\nu}^{\rho} \Gamma_{\mu\sigma}^{\kappa} - \Gamma_{\kappa\sigma}^{\rho} \Gamma_{\mu\nu}^{\kappa} \right),$$

all terms with $\Gamma_{\nu\alpha}^{\mu}$ and $\frac{\partial}{\partial x^{\lambda}} \Gamma_{\nu\alpha}^{\mu}$ vanish in x_0^{ν} , and only the following expression remains :

$$\begin{aligned} \frac{\partial^2}{\partial x^{\tau} \partial x^{\nu}} \Gamma_{\mu\sigma}^{\rho} - \frac{\partial^2}{\partial x^{\tau} \partial x^{\sigma}} \Gamma_{\mu\nu}^{\rho} + \frac{\partial^2}{\partial x^{\nu} \partial x^{\sigma}} \Gamma_{\mu\tau}^{\rho} - \frac{\partial^2}{\partial x^{\nu} \partial x^{\tau}} \Gamma_{\mu\sigma}^{\rho} \\ + \frac{\partial^2}{\partial x^{\sigma} \partial x^{\tau}} \Gamma_{\mu\nu}^{\rho} - \frac{\partial^2}{\partial x^{\sigma} \partial x^{\nu}} \Gamma_{\mu\tau}^{\rho}, \end{aligned}$$

which vanishes identically. Hence also (1) vanishes identically.

Yours faithfully,
J. A. SCHOUTEN,
D. J. STRUIK.

Delft, April 28, 1923.

P.S. February 7, 1924.—A generalization of Bianchi's identity for a geometry with a non-symmetrical displacement is found in Weitzenböck, *Invariantentheorie* (P. Noordhoff, Groningen, 1923, p. 357). The above given proof of the identity occurs also in the quoted paper of Veblen. For a generalization for the geometry with the most general linear displacement see the book of Schouten, '*Der Ricci-Kalkül*,' that will soon appear in Springer's series: *Die Grundlehren der mathematischen Wissenschaften*.

LII. *On the Origin of certain Spectral Lines hitherto attributed to Oxygen.* By W. JEVONS, A.R.C.Sc., M.Sc.,
Lecturer in Physics, Artillery College, Woolwich*.

CERTAIN lines in the ultra-violet have been attributed by Schniederjost† to the so-called "compound line spectrum" of oxygen, which is now known as O.I‡ and ascribed to the neutral atom of oxygen. Professor Fowler in his Report§ makes the following reference to these lines:— "A considerable number of lines of O.I have been observed in the ultra-violet by Schniederjost, but their relation to the established series, if any, has not yet been traced. The wave-lengths of these lines are included in the table of unclassified lines"||. It is the object of this paper to offer new evidence as to the origin of these lines, concerning which Schniederjost would seem to have been misled.

In the course of an investigation of the ultra-violet line spectrum of chlorine by the present writer¶, a number of well-defined bands were observed in the condensed discharge through a chlorine tube which was known to contain carbon, hydrogen and oxygen as impurities. The heads of these bands degraded towards the red, and their line-structure was clearly shown. A close agreement of wave-length was found between these band-heads and some of the more refrangible of Schniederjost's O.I lines, and some doubt was felt, therefore, as to the real existence of the latter. An attempt was then made to observe them in the oxygen spectrum. For this observation a continuous flow of oxygen, prepared by the electrolysis of barium hydroxide solution and dried by phosphorus pentoxide, was passed through a length of capillary tube, then through a discharge-tube with a quartz window end-on to the capillary, and finally to a pump which was kept in action throughout each exposure in a

* Communicated by Professor E. N. da C. Andrade.

† *Zeit. f. Wiss. Phot.*, ii. p. 283 (1904). See also Kayser, *Handbuch der Spectroscopie*, vi. p. 213.

‡ Fowler and Brooksbank, *R. A. S. Mon. Not.*, lxxvii. p. 513 (1917).

§ "Report on Series in Line Spectra," *Phys. Soc. Lond.*, p. 167 (1922).

|| In Prof. Fowler's table (*loc. cit.* p. 169) Schniederjost's wave-lengths have been converted to the International Scale. This table has been employed, together with the vacuum corrections given by Meggers and Peters [*Sci. Papers*, B. of S. Washington, No. 327 (1918)] in deriving the wave-numbers ν_{vac} in column 4 of Table I.

¶ *Roy. Soc. Proc.*, A, ciii. p. 193 (1923).

small Hilger quartz prism spectrograph. Though lines of the established O.I series * were well developed, only one line was detected in a position given in Schniederjost's O.I list (Table I. column 3), namely $\lambda_{\text{R.A.}} 2883.93$ (4), which is also given as an oxygen line by Runge and Paschen † at $\lambda_{\text{R.A.}} 2883.95$ (6). Prof. Fowler's oxygen observations ‡ not only confirm this result, but also indicate that $\lambda_{\text{R.A.}} 2883.93$ may be an enhanced (O II) rather than an O.I line.

The observed bands already mentioned have now been recognized as some of Deslandres' First Negative bands of carbon §. The close agreement between Deslandres' and Schniederjost's wave-lengths in columns 1 and 3 of Table I. leaves little doubt as to the identification of sixteen of Schniederjost's lines with Deslandres' band-heads.

Three of Schniederjost's wave-lengths not thus correlated show some agreement with those of three band-heads (in column 2) belonging to another of Deslandres' carbon band-systems, namely the Fourth Positive ||. The agreement is not so good as in the case of the First Negative bands, owing perhaps to the lesser degree of accuracy attainable at the time of the pioneer measurements (1888).

If these identifications be accepted there remain only five of Schniederjost's measures to be accounted for; namely $\nu\nu 34529.1$, 34691.1 , 34970.7 , 36915.6 , 37403.0 (see Table I. column 4). The question of these may be approached, and at the same time the band-like distribution of the majority of Schniederjost's "lines" be demonstrated, by arranging the wave-numbers (column 4) in the manner first employed by Deslandres for the First Negative and other band systems, and subsequently by many other observers. The scheme is such that the first differences of the wave-numbers form arithmetical progressions in horizontal rows and vertical

* See Tables in Prof. Fowler's Report, pp. 167 & 168. Paschen and Götzke, 'Seriengesetze der Linienspektren' (Berlin, 1922), pp. 136-138; and W. M. Hicks, 'Analysis of Spectra' (C.U.P. 1922), pp. 298 & 299.

† *Ann. d. Phys.*, lxi. p. 647 (1897); *Astrophys. Journ.*, viii. p. 70 (1898). See also Kayser's *Handbuch*, vi. p. 213.

‡ Unpublished but kindly placed at the author's disposal by Professor Fowler.

§ H. Deslandres, *Comptes Rendus*, cxxxvii. p. 460 (1903); see also Kayser's *Handbuch*, v. p. 233.

|| H. Deslandres, *Comptes Rendus*, cvi. p. 842 (1888); *Annales de Chim. et de Phys.*, (6) xv. p. 85 (1888). See also Kayser's *Handbuch*, v. p. 233.

TABLE I.

1	2	3	4	5	6	7
Heads of First Negative Bands. (Deslandres.)	Heads of Fourth Positive Bands. (Deslandres.)	O.I Lines (Schniederjost).				Notes.
$\lambda_{R.A.}$ Int.	$\lambda_{R.A.}$ Int.	$\lambda_{R.A.}$ Int.	$\nu_{vac.}$ $= 10^8/\lambda_{I.A. vac.}$	Group n p (See Table II.)	$\nu_{obs.}$ $-\nu_{calc.}$	
2897.11 10		2897.42 2n	34504.7			a
		95.37 3	34529.1			
83.86 10		83.93 4	34666.1			a, b
		81.85 2n	34691.1	II 67 32	+4.3	
		58.81 1	34970.7			
2786.51 1		2786.17 1	35882.3	IV 66 30	+1.0	
53.65 1		53.47 1	36308.5	III 67 31	-1.5	
23.06 3		22.57 1	36720.5	II 68 32	+2.3	c
		08.18 1	36915.6			
2694.80 2				I 69 33		d
		2672.89 1	37403.1	V 66 29	-0.7	
39.63 4		39.00 2	37883.3	IV 67 30	+0.5	
07.95 4		07.51 2	38340.7	III 68 31	-0.6	
2578.39 6		2577.93 2	38780.9	II 69 32	+1.5	
51.20 5		50.64 1	39195.5	I 70 33	-1.6	
05.39 3		04.67 2	39914.8	IV 68 30	+0.7	
2475.10 4		2474.45 2	40402.1	III 69 31	-0.5	
46.69 8		46.05 3	40871.2	II 70 32	+0.6	
20.29 8		19.64 3	41317.3	I 71 33	-0.8	
2353.23 4		2352.61 2	42494.4	III 70 31	+0.7	e
25.93 7		23.34 2	42992.7	II 71 32	+1.1	
2300.36 7		2299.93 3	43467.5	I 72 33	-1.5	
	2215.3 10	14.62 2	45141.8	II 72 32	-0.7	
2190.51 4		2189.99 2	45649.4	I 73 33	-0.4	
	2136.5 2	37.6 1	46768.8			
	12.7 8	12.4 1	47326.7	II 73 32	-3.4	

Notes to Table I. (column 7.)

(a) Deslandres points out that these two bands differ from the remainder in two respects: (i.) the two strong heads are degraded in both directions, while the others are degraded towards the red, and (ii.) they cannot be included in the same group scheme (see Table II.) with the others.

(b) Also observed as an oxygen line by Runge and Paschen (*loc. cit.*), Professor Fowler, and the author.

(c) The measure published by Schniederjost is $\lambda_{R.A.}$ 2723.57, whence $\nu_{vac.} = 36707.0 \text{ cm.}^{-1}$. There is, however, some reason (which will become clear from Table II.) for believing that this wave-length is 1 unit too high. The modified value has been entered in this table. The difference from Deslandres' corresponding wave-length is not thereby altered in magnitude but only in sign, and the sign is brought into agreement with that of the corresponding differences ($\lambda_{Desl.} - \lambda_{Schn.}$) for the other heads.

(d) For easy reference to Table II. it may be noted here that the wave-number derived from Deslandres' λ for this head is $\nu_{vac.}$ 37098.8.

(e) Given by Miss G. V. Morrow [*Sci. Proc. Roy. Dublin Soc.*, xiii. p. 615 (1913)] as $\lambda_{R.A.}$ 2352.6 (4), with a note that, though the line has been attributed to gold, it is more probably due to oxygen. It may be noted here also, that the line $\lambda_{R.A.}$ 2478.7 (5) attributed to oxygen by Miss Morrow is really a well-known carbon line.

n (column 3)=nebulous

columns, as in Table II. in which Deslandres' numbers I-IV for the vertical groups are retained.

TABLE II.

Group:—	I	II	III	IV	V
<i>p</i>	33	32	31	30	29
<i>n</i>	(2)	(1)			
73	45649.4 1677.3	47326.7 ^g			
	2189.9	2184.9			
	(3)	(2)			
72	45467.5 1674.3	45141.8 ^g			
	2150.2	2149.1			
	(3)	(3)			
71	41317.3 1675.4	42992.7			
	2121.8	2121.5			
	(1)	(3)	(-)		
70	39195.5 1675.7	40871.2 1623.2	42494.4		
	2069.5	2090.3	2092.3		
	(2)	(2)			
69	[57106.0] 1674.9	38780.9 1621.2	40402.1		
		2060.4	2061.4		
		(1) <i>c</i>	(2)	(2)	
68		36720.5 1620.2	38340.7 1574.1	39914.8	
		2029.4	2032.2	2031.5	
		(2 <i>a</i>)	(1)	(2)	
67		34691.1 1617.4	36308.5 1574.8	37883.3	
			2001.0		
			(1)	(1) <i>f</i>	
66			35882.3 1520.7	37403.0	

Notes to Table II.

() Intensities by Schmiederjost.

c Modified value of ν_{vac} , used instead of 35707.0 (see note *c* to Table I.).

d Not observed by Schmiederjost. The value of ν_{vac} , from Deslandres' observation is 37098.8 (see note *d* to Table I.).

[] Computed ν_{vac} , (formula, page 590).

f Not observed by Deslandres.

g Not observed as First Negative band-heads by Deslandres, who, however, gives Fourth Positive band-heads at about these positions (see Table I. column 2).

From this table the following conclusions may be drawn:—

1. One of the five outstanding wave-numbers, namely $\nu 37403.0$, represents a previously unobserved head, falling in a new group (V) of the extended Deslandres' First Negative system.

2. Another of them, namely $\nu 34691.1$, probably represents an extension of Group II; the slight discrepancies in intensity and wave-number being due perhaps to the nebulous character of the observed "line."

3. The remaining three $\nu \nu 34529.1$, 34970.7 , and 36915.6 appear to be definitely excluded from the First Negative carbon system.

4. There is a possible alternative allocation of two of the three measures, which have been already correlated (page 587) with three of Deslandres' Fourth Positive band-heads.

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These two are $\nu\nu 45141\cdot8$ and $47326\cdot7$, which are shown as a possible extension of Group II.

Schniederjost's wave-numbers in Table II. are very closely represented by an empirical formula of the type commonly employed for band systems, namely :—

$$\nu = 14\cdot944 (n + 0\cdot4655)^2 - 25\cdot177 (p + 0\cdot7344)^2 - 6354\cdot0$$

in which n and p take successive integral values, the former from 66 to 73, and the latter from 29 to 33, as shown in both tables. The residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) are given in Table I. (column 6).

In conclusion, then, it seems almost certain that, of Schniederjost's twenty-five O.I observations twenty-one are not to be associated with oxygen at all but are good measures of Deslandres' carbon band-heads in the same region. carbon being a very frequent impurity in discharge tubes. $\lambda_{\text{R.A.}}$ 2883·93 is a genuine oxygen line confirmed by the observations of Runge and Paschen, Prof. Fowler, and the present writer. The three at $\lambda_{\text{R.A.}}$ 2895·37, 2858·81, and 2708·18 may still be regarded as lines, at least pending a further investigation of the bands.

The possibility of confusion between lines and band-heads (which is liable to arise where the source is at a low pressure and the band-heads are only faintly recorded on the plate) was perhaps not so well known at the time of Schniederjost's work as it is now. The modification of intensities in the line-structure of a band as observed under some conditions is often such that a band-head resembles a line winged on one side*.

Finally, it may be noted that this communication is concerned only with the O.I observations of Schniederjost, and has no reference to the O.II lines† (of the "elementary line" spectrum) measured by him. The latter have, in the main, been confirmed and amplified by Professor Fowler.

I am greatly indebted to Prof. E. N. da C. Andrade for his help and interest and for many facilities, including the unrestricted use of the spectroscopic apparatus in the Physics Department of the Artillery College. I also wish to thank Prof. A. Fowler for kindly allowing me to make use of his unpublished oxygen data and for many helpful suggestions.

* For a plate illustrating this effect in silicon nitride bands, for instance, see: W. Jevons, Roy. Soc. Proc., A, lxxxix. plate 9, p. 193 (1913).

† *Loc. cit.* p. 283; see also Kayser's *Handbuch*, vi. p. 218.

LIII *On the Helmholtz Theories of the Struck String.*—
Part I. *Theoretical.* By W. H. GEORGE, B.Sc., *Research*
Student, University College, Nottingham *.

[Plate III.]

SUMMARY.—The various theoretical treatments of the struck string are noted, and the Helmholtz theory for the hard hammer is then considered in detail, and is shown to be in conflict with experimental evidence. The Helmholtz theory for the elastic hammer is next considered, with the omission of two assumptions which caused Kaufmann to reject the theory. Expressions are found for quantities whose magnitude can be determined from photographically obtained displacement-time curves of the struck point. Expressions for the same quantities are derived from Kaufmann's theory of the string struck at the mid-point, and also from Kaufmann's approximate theory of the string struck near one end. The comparison of the theoretically and experimentally determined quantities is to be given in the second part of the paper.

INTRODUCTION.

THE problem of the struck string has been theoretically treated by two methods. Helmholtz †, Delemer ‡, and Lamb § each assume some special form for the pressure between the hammer and the string during the time of contact. Proceeding from the assumed pressure-time laws and using some additional assumptions, each of these writers obtains finally an expression giving the intensities of the partials of the freely vibrating string. None of these treatments which illustrate the first method appears to have been subjected to quantitative experimental tests.

The second method of treatment is that due to Kaufmann ||, who considers the problem of the impact of a massive *unyielding* particle on the string. He gives a rigorous treatment for the string of infinite length, and also for the finite string struck at the middle point, provided, in this second case, that the time of contact between hammer and string is not greater than the fundamental free period of the string. In an attempt to simplify the work, he treats the case of the

* Communicated by Prof. E. H. Barton, F.R.S.

† Helmholtz, 'Sensations of Tone,' pt. i. Chap. v. § 3, and App. v.

‡ Delemer, *Annal. Soc. Sci. de Bruxelles*, xxx. 3 & 4, pp. 299-310 (1905-6).

§ Lamb, 'Dynamical Theory of Sound,' p. 74.

|| Kaufmann, *Wied. Ann.* vol. liv. pp. 675-712 (1895).

string struck near one end by neglecting the vibrations of the shorter piece of string during the impact, obtaining an approximate solution for the case in which the ratio of the time of contact to the free period of the string is not greater than the ratio of the distance of the struck point from the farther bridge to the length of the string. Das* has repeated this work, taking into account the vibrations of the shorter piece of string, but with the same limitation as to the time of contact. Kaufmann gives no treatment for a string struck at, say, one-third of its length from one end. Raman and Banerji† have extended Kaufmann's work by regarding the motion during impact as that of a loaded string to which Rayleigh's well-known treatment may be applied.

In the present paper an attempt is made at the quantitative experimental test of the Helmholtz theories and their comparison with the Kaufmann theory in those cases to which the latter theory may be applied.

HELMHOLTZ THEORY FOR THE HARD HAMMER.

In considering the problem of a string struck at a point with a hard hammer, Helmholtz observed:—"If the string is struck with a sharp-edged metallic hammer which rebounds instantly, only the one single point struck is directly set in motion. Immediately after the blow the remainder of the string is at rest. It does not move until a wave of deflexion rises and runs backwards and forwards over the string" (*loc. cit.* p. 75.) In order that these conditions may be realized, it is clear that the impact must last for only a very small fraction of the period of the string. It was found by Kaufmann that the time of contact was always comparable with the period of the string, and he therefore rejected the theory without further consideration. As, however, this theory is still quoted in most of the standard text-books, it would appear that Kaufmann's observation has been overlooked. In the present paper (Pl. III. figs. 1 & 2) it will be seen that, although the time of contact (τ) is less than in any of Kaufmann's experiments, it is still comparable with the period (θ) of the string. For example, in fig. 1 we see that τ/θ is of the order one-seventh, so that the transverse disturbance has during the impact travelled a distance of

* Das, Proc. Indian Assoc. for the Cultivation of Science, vol. vii. pts. i. & ii. pp. 13-20 (1921).

† Raman & Banerji, Proc. Roy. Soc. vol. xcvi. A, pp. 99-110 (1920).

about 90 cm. towards the farther bridge, and has travelled the short distance of 12 cm. to the nearer bridge more than seven times, involving three reflexions at the hammer.

In considering this theory of Helmholtz, it is sometimes supposed that in an actual experiment the hammer strikes and rebounds, leaving a small wrinkle on the string at the struck place. It is helpful to consider the order of magnitude of the quantities involved. On a string 100 cm. long, tuned to a frequency of 128 vibns. per sec., the velocity of propagation of transverse waves is 12,800 cm. per sec., whilst the initial hammer velocity usually employed in experiments on the struck string lies between 100 and 500 cm. per sec. It is clear that this "wrinkle" supposition implies that not only is the time of contact negligibly small compared with the free period of the string, but also that the initial velocity of the hammer is *greater* than the speed of propagation of transverse disturbances along the string. The actual form of the string in the neighbourhood of the struck point is shown in Pl. III. figs. 3 & 4. These are instantaneous photographs of the hammer and string, taken during the impact. Fig. 3 shows a metallic hammer of very small breadth at the place of contact, whilst fig. 4 shows a felt-covered hammer in contact over a distance of about 1.2 cm. A pin was stuck in the felt hammer-head so that it was approximately perpendicular to the direction of approach of the hammer. The string, when at rest, passes through the two pin points shown at the top of the figure. On the actual film from which fig. 3 was taken the bridges are shown, and from these the undisplaced position of the string is readily obtained*.

Helmholtz elsewhere (*loc. cit.* Appendix v.) states that the hammer must be immediately withdrawn. In this respect a recent paper by S. Hayashi † is of interest, as a spring device for withdrawing the hammer is there described. The shortest time of contact shown in the reproduced displacement-time photographs is, however, of the order one-third of the period of the string; that is, longer than in a number of the experiments described in Kaufmann's paper or in the

* To study experimentally the forms assumed by vibrating strings, both loaded and unloaded, when excited by various means, the method of instantaneous photography has been used. The experimental details, together with the results obtained, will be published later. The two figures given in this paper are typical examples of the photographs of the struck string during the impact.

† S. Hayashi, *Kyoto Coll. Sci. Mem.* vi. pp. 165-169 (March 1923).
Phil. Mag. S. 6. Vol. 47. No. 279. March 1924. 2 Q

present paper. There are no other recorded experiments in which any device for withdrawing the hammer has been used.

We may therefore conclude that this theory is inapplicable to the experimental results so far published.

HELMHOLTZ'S THEORY FOR THE ELASTIC HAMMER.

In order to treat the problem of a string struck with a felt-covered hammer, Helmholtz (*loc. cit.* Appendix v.) observed that "the elastic pad yields to the blow at first and then recovers itself, so that while the hammer is in contact with the string, the motion is capable of extending over a considerable length Observing that the string moves but very slightly from its position of rest, and that the elastic pad of the hammer is very yielding and admits of much compression, we may simplify the mathematical theory, by assuming the pressure exerted by the hammer during the blow which it gives to the string to be $P = A \sin \pi t / \tau$," where t = variable time, τ = duration of contact, and A is a constant which may be seen to be the value of the pressure when $t = \tau/2$. With the aid of an additional assumption as to the time of contact, Helmholtz obtains finally an expression giving the amplitude of the partials in the tone of the freely vibrating string.

Kaufmann rejected this theory because he concluded that (i.) the elasticity of the hammer is a negligible factor compared with the tension of the string in causing the rebound of the hammer, and (ii.) $(\tau/\theta) > (a/l)$ whilst Helmholtz had assumed that $(\tau/\theta) < (a/l)$. It is clear, however, that the original assumption of the pressure law is not explicitly dependent on either of these two assumptions, and the purpose of the remainder of the present paper is a reconsideration of this Helmholtz theory, with the omission of the two assumptions which are in conflict with Kaufmann's experimental work. Since the displacement-time curve of the struck point can be so conveniently obtained by the photographic method due to A. Rafs and O. Krigar-Menzel*, we proceed to derive from the Helmholtz pressure law expressions for quantities whose magnitude can be readily determined from such a curve.

* A. Rafs and O. Krigar-Menzel, *Wied. Ann.* vol. xlv. p. 623 (1891).

THEORY.

Notation :—

- l = length of string (in cm.).
- a = distance of struck point from nearer bridge (in cm.).
- b = distance of struck point from farther bridge (in cm.).
- y = variable displacement of struck point reckoned positive in the direction of the approaching hammer (in cm.).
- y_1 = displacement of struck point at the instant of separation of hammer and string (in cm.).
- y_2 = maximum displacement of struck point (in cm.).
- r = distance between string and axis of rotation of hammer (in cm.).
- θ = free period of fundamental tone of string (in sec.).
- τ = duration of impact (in sec.).
- t = variable time reckoned from the instant of the beginning of the impact (in sec.).
- t_2 = time taken for y to reach its maximum value (in sec.).
- v_0 = initial velocity of hammer (in cm. per sec.).
- v = velocity of hammer at instant of separation of hammer and string (in cm. per sec.).
- μ = linear density of string (in gm. per cm.).
- m = mass of hammer (see following note).
- M = mass of string = μl (in gm.).

The actual hammer under consideration may be regarded as a compound pendulum. By the term "*mass of hammer*" is meant the mass in gm. of a particle equimomental with the hammer and distant r from the axis of rotation of the pendulum; that is, the moment of inertia of the pendulum about its axis of rotation is mr^2 . We assume that the motion takes place in one plane passing through the string. For the force on the hammer we may write

$$m \frac{d^2 y}{dt^2} = -A \sin \frac{\pi t}{\tau} \quad . \quad . \quad . \quad . \quad (1)$$

$(0 < t < \tau)$

Hence

$$\int_{v_0}^{\frac{dy}{dt}} d\left(\frac{dy}{dt}\right) = -\frac{A}{m} \int_0^t \sin \frac{\pi t}{\tau} \cdot dt.$$

It will be noted that we have put $\frac{dy}{dt} = v_0$ when $t = 0$. If this be regarded as an assumption, it can be seen to be clearly justifiable by an examination of the experimentally

obtained displacement-time curves accompanying this paper. Integrating, we have

$$\frac{dy}{dt} = v_0 + \frac{A}{m} \cdot \frac{\tau}{\pi} \left(\cos \frac{\pi t}{\tau} - 1 \right). \quad (2)$$

($0 < t < \tau$)

By putting $t = \tau/2$ in equation (1), we see that the Helmholtz constant A is the value of the force exerted by the hammer on the string when $t = \tau/2$. As this quantity is not readily determined by experiment, we may eliminate it from the equations by introducing a new quantity—the velocity of rebound (v) of the hammer which has not hitherto been considered in the study of the struck string. It may be noted in passing that the writer hopes to study the energy aspect of the general problem by the aid of this quantity, since in the ideal case the energy absorbed by the vibrating system is $\frac{1}{2}m(v_0^2 - v^2)$. By putting $t = \tau$ in equation (2), we find

$$v = v_0 - \frac{2A\tau}{\pi m}, \quad (3)$$

or
$$A = \frac{m\pi}{2\tau} (v_0 - v). \quad (3a)$$

Hence equation (2) may be rewritten thus :

$$\frac{dy}{dt} = \frac{1}{2} \left[(v_0 + v) + (v_0 - v) \cos \frac{\pi t}{\tau} \right]. \quad (2a)$$

($0 < t < \tau$)

Integrating again and putting in the condition that $y = 0$ when $t = 0$, we have

$$y = \frac{1}{2} \left[(v_0 + v)t + \frac{\tau}{\pi} (v_0 - v) \sin \frac{\pi t}{\tau} \right]. \quad (4)$$

($0 < t < \tau$)

By putting $t = \tau$ in this equation, we see that the displacement of the struck point at the instant of separation of hammer and string is given by

$$y_1 = \frac{\tau}{2} (v_0 + v). \quad (5)$$

When the string under considerable tension is struck by a light hammer near one of the bridges, the actual displacements of the struck point are so small that it is almost useless to attempt to measure any but the maximum value

(y_2) of the displacement. Observing that the hammer is then instantaneously at rest, we obtain the time (t_2) for y to reach its maximum value from equation (2 a) by putting $dy/dt=0$. Hence

$$t_2 = \frac{\tau}{\pi} \left\{ \pi - \cos^{-1} \left(\frac{v_0 + v}{v_0 - v} \right) \right\} \quad . \quad . \quad . \quad (6)$$

Putting this value in equation (4), we obtain

$$y_2 = \frac{\tau}{2\pi} \left\{ (v_0 + v) \left[\pi - \cos^{-1} \left(\frac{v_0 + v}{v_0 - v} \right) \right] + 2 \sqrt{-vv_0} \right\} \quad . \quad (7)$$

By use of a planimeter the area between the curve and the axis of time may be conveniently measured, and is given by

$$\int_0^t y \, dt = \frac{1}{2} \left[\frac{1}{2} (v_0 + v) t^2 + \frac{\tau^2}{\pi^2} (v_0 - v) \left(\cos \frac{\pi t}{\tau} - 1 \right) \right] \quad . \quad (8)$$

In the special case when t reaches its maximum value of τ , we have

$$\int_0^\tau y \, dt = \tau^2 \left[\frac{1}{4} (v_0 + v) + \frac{1}{\pi^2} (v_0 - v) \right] \quad . \quad . \quad (9)$$

We proceed to compare these results with those derived from Kaufmann's theory.

COMPARISON WITH KAUFMANN'S THEORY FOR A STRING STRUCK AT THE MID-POINT.

The Kaufmann equations * for this case, which, it may be noted, hold only if the time of contact is less than one period of the string, run as follows:—

$$y = v_0 \theta \frac{m}{4M} \left(1 - e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \right), \quad . \quad . \quad . \quad (10)$$

$$\left(0 < \frac{t}{\theta} < \frac{1}{2} \right)$$

$$y = v_0 \theta \left\{ e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \left[2e^{\frac{2M}{m} \left(\frac{t}{\theta} - \frac{1}{2} + \frac{m}{4M} \right)} - \frac{m}{4M} \right] - \frac{m}{4M} \right\},$$

$$\left(\frac{1}{2} < \frac{t}{\theta} < 1 \right) \quad . \quad . \quad . \quad (11)$$

$$\frac{\tau}{\theta} = \frac{1}{2} + \frac{1}{4} \frac{m}{M} \left(1 + \frac{1}{2} e^{-\frac{2M}{m}} \right) \quad . \quad . \quad . \quad (12)$$

* There are some printer's errors on p. 688 of Kaufmann's paper, and both forms of the final equation are given wrongly. Equation (11), as here given, will be found to agree with Kaufmann's own numerical calculations.

Differentiating (10) and (11) each once with respect to time, we obtain

$$\frac{dy}{dt} = v_0 e^{-\frac{4M}{m} \cdot \frac{t}{\theta}}, \quad \dots \quad (13)$$

$$\left(0 < \frac{t}{\theta} < \frac{1}{2}\right)$$

$$\begin{aligned} \frac{dy}{dt} = v_0 e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \left\{ -\frac{4M}{m} \left[2e^{\frac{2M}{m} \left(\theta - \frac{1}{2} + \frac{m}{4M} \right)} - \frac{m}{4M} \right] \right. \\ \left. + 2e^{\frac{2M}{m}} \right\}. \quad (14) \end{aligned}$$

Combining equations (14) and (12), we obtain the velocity of rebound of the hammer :

$$v = -2v_0 e^{-\left(1 + \frac{1}{2} e^{-\frac{2M}{m}}\right)}. \quad \dots \quad (15)$$

The pressure law can be derived from equations (13) and (14) by differentiating each once more with respect to time and then multiplying by the mass of the hammer :

$$m \frac{d^2 y}{dt^2} = -v_0 \frac{4M}{\theta} e^{-\frac{4M}{m} \cdot \frac{t}{\theta}}, \quad \dots \quad (16)$$

$$\left(0 < \frac{t}{\theta} < \frac{1}{2}\right)$$

$$\begin{aligned} m \frac{d^2 y}{dt^2} = -v_0 \frac{8M}{\theta} e^{\frac{2M}{m} \left(1 - \frac{2t}{\theta}\right)} - v_0 \frac{4M}{\theta} e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \left\{ -\frac{4M}{m} \times \right. \\ \left. \left[2e^{\frac{2M}{m} \left(\theta - \frac{1}{2} + \frac{m}{4M} \right)} - \frac{m}{4M} \right] + 2e^{\frac{2M}{m}} \right\}. \quad (17) \end{aligned}$$

The displacement (y_1) of the struck point at the instant of separation of hammer and string is found from equations (11) and (12) to be

$$y_1 = v_0 \theta \frac{m}{M} \left[e^{-\left(1 + \frac{1}{2} e^{-\frac{2M}{m}}\right)} - \frac{1}{4} \right]. \quad \dots \quad (18)$$

The time taken for y to reach its maximum value (y_2) is found by equating the right-hand side of equation (14) to zero. Whence

$$t_2 = \frac{\theta}{2} \left(1 + \frac{1}{4} \frac{m}{M} e^{-\frac{2M}{m}} \right). \quad \dots \quad (19)$$

Hence

$$y_2 = \frac{v_0 \theta m}{4M} \left\{ 2e^{-\left(\frac{1}{2} e^{-\frac{2M}{m}}\right)} - 1 \right\}. \quad \dots \quad (20)$$

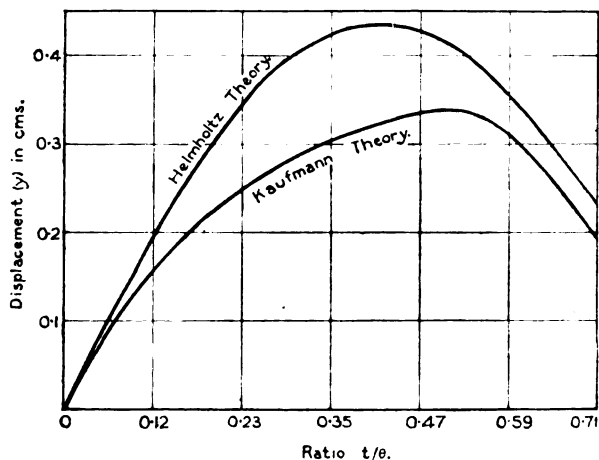
The area contained between the curve and the axis of time is the sum of two parts which have to be determined separately from equations (10) and (11). We have from equation (10)

$$\int_0^t y dt = v_0 \theta \frac{m}{4M} \left(\int_0^t dt - \int_0^t e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} dt \right) \\ (0 < \frac{t}{\theta} < \frac{1}{2}) = v_0 \theta \frac{m}{4M} \left[t + \frac{\theta m}{4M} \left(e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} - 1 \right) \right], \quad (21)$$

and from equation (11)

$$\int_{\frac{1}{2}}^t y dt = v_0 \theta \left\{ \frac{2}{\theta} e^{-\frac{2M}{m}} \int_{\frac{1}{2}}^t t e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} dt + \left[e^{-\frac{2M}{m}} \left(\frac{m}{2M} - 1 \right) - \frac{m}{4M} \right] \int_{\frac{1}{2}}^t e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} dt - \frac{m}{4M} \int_{\frac{1}{2}}^t dt \right\} \\ = v_0 \theta \left\{ \frac{\theta}{8} \cdot \frac{m^2}{M^2} e^{-\frac{2M}{m}} \left[e^{-\frac{2M}{m}} \left(\frac{2M}{m} + 1 \right) - e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \left(\frac{4M}{m} \cdot \frac{t}{\theta} + 1 \right) \right] \right\} \\ + v_0 \theta \left\{ \left[e^{-\frac{2M}{m}} \left(\frac{m}{2M} - 1 \right) - \frac{m}{4M} \right] \left(e^{-\frac{2M}{m}} - e^{-\frac{4M}{m} \cdot \frac{t}{\theta}} \right) \frac{m\theta}{4M} - \frac{m}{4M} \left(t - \frac{\theta}{2} \right) \right\} \quad \dots \quad (22)$$

Fig. 1.



Theoretical displacement-time curves for the struck point.

$M=4.8$; $m=4.4$; $\theta=1/128$; $\tau\theta=0.74$; $v_0=215$; $v=-149$; $l/a=2$.

COMPARISON WITH KAUFMANN'S THEORY FOR A STRING
STRUCK NEAR ONE END.

Kaufmann's equations for this case run thus :—

$$\left(0 < \frac{t}{\theta} < \frac{b}{l}\right) \frac{y}{r_0 \theta} = \frac{1}{\sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)}} e^{-\frac{M}{m_0} \cdot \frac{t}{\theta}} \times \sin \left\{ \frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)} \right\}, \quad (23)$$

and

$$\frac{\tau}{\theta} = \frac{1}{\sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)}} \tan^{-1} \left\{ \frac{\sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)}}{-2 \frac{l}{a} + \frac{M}{m_0}} \right\}. \quad (24)$$

The approximations used by Kaufmann have already been noted in the introduction to this paper, and the quantity m_0 is defined thus: $m_0 = m + \mu a/3$ —that is, to the mass of the hammer (m) is added the mass of a particle which, if placed on the struck point, would be equimomental with the shorter piece of string (of length a) so far as rotations about the nearer bridge are concerned. It will be recalled that Kaufmann assumes that this shorter piece of the string remains uncurved during the period of impact.

We proceed, as before, to derive from these equations the special quantities required.

At the instant of separation of hammer and string we have

$$y_1 = \frac{a}{2l} r_0 \theta e^{-\frac{M}{m_0} \cdot \frac{1}{\sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)}} \tan^{-1} \left\{ \frac{\sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)}}{-2 \frac{l}{a} + \frac{M}{m_0}} \right\}}. \quad (25)$$

From equation (23) we have

$$\begin{aligned} \frac{dy}{dt} = & \frac{r_0 e^{-\frac{M}{m_0} \cdot \frac{t}{\theta}}}{\sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)}} \cdot \left\{ \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)} \right. \\ & \times \cos \left[\frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)} \right] \\ & \left. - \frac{M}{m_0} \sin \left[\frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0}\right)} \right] \right\} \quad (26) \end{aligned}$$

Hence the velocity of rebound is given by

$$v = -v_0 e^{-\frac{M}{m_0} \cdot \frac{1}{\sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)}} \tan^{-1} \left\{ \frac{\sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)}}{-2 \frac{l}{a} + \frac{M}{m_0}} \right\}}. \quad (27)$$

The time (t_2) taken for y to reach its maximum value is found from equation (26) to be

$$t_2 = \frac{\theta}{\sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)}} \tan^{-1} \left[\frac{m_0}{M} \sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)} \right]. \quad (28)$$

Hence the maximum displacement (y_2) of the struck point is given by

$$y_2 = v_0 \theta \sqrt{\frac{1}{4} \frac{a}{l} \frac{m_0}{M}} \cdot e^{-\frac{M}{m_0} \cdot \frac{1}{\sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)}} \tan^{-1} \left(\sqrt{\frac{m_0}{M} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)} \right)} \quad (29)$$

The pressure law is obtained from equation (26) :

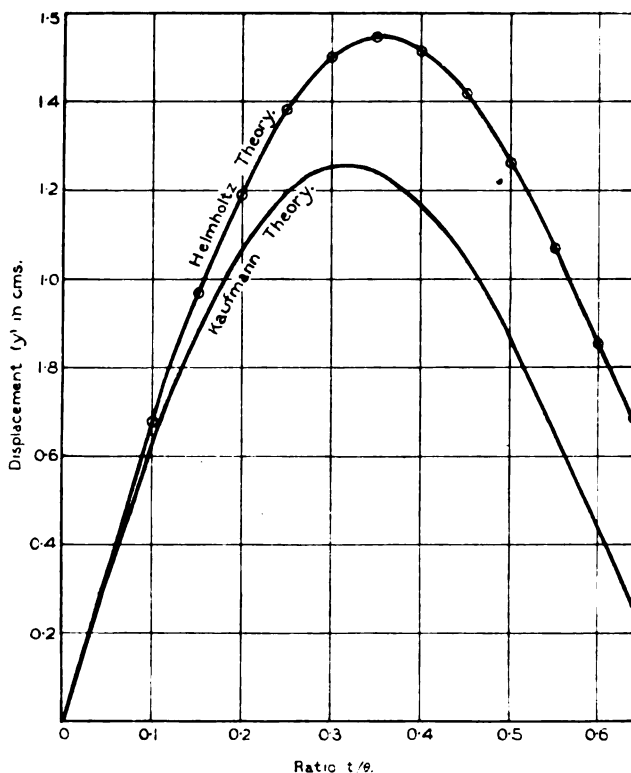
$$\begin{aligned} m_0 \frac{d^2 y}{dt^2} &= \frac{2 M v_0 e^{-\frac{M}{m_0} \cdot \frac{t}{\theta}}}{\theta \sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)}} \left\{ \left(\frac{M}{m_0} - \frac{2l}{a} \right) \right. \\ &\times \sin \left[\frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)} \right] - \sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)} \\ &\times \cos \left[\frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)} \right] \left. \right\} \dots \dots \dots (30) \end{aligned}$$

Finally the area between the curve and the axis of time is found from equation (23) by integrating by parts and solving for the desired integral, whence

$$\begin{aligned} \int_0^t y dt &= \frac{v_0}{\sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)}} \frac{\theta^2 a m_0}{4 l M} \left\{ \sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)} \right. \\ (0 < \frac{t}{\theta} < \frac{l}{a}) & - e^{-\frac{M t}{m_0 \theta}} \left[\frac{M}{m_0} \sin \left\{ \frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)} \right\} \right. \\ & \left. \left. + \sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)} \cos \left\{ \frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(4 \frac{l}{a} - \frac{M}{m_0}\right)} \right\} \right] \right\}. \quad (31) \end{aligned}$$

The comparison of the theoretically and experimentally determined quantities will be given in the second part of the paper.

Fig. 2.



Theoretical displacement-time curves for the struck point.

$M=29.4$; $m=49.5$; $m_0=50.6$; $\theta=1/47$; $\tau/\theta=0.64$; $v_0=325$;
 $v=-224$; $l/a=9$.

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University College, Nottingham,
 Dec. 1923.

Hence the velocity of rebound is given by

$$v = -v_0 e^{-\frac{M}{m_0} \cdot \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \tan^{-1} \left\{ \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \right\}} \quad (27)$$

The time (t_2) taken for y to reach its maximum value is found from equation (26) to be

$$t_2 = \frac{\theta}{\sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)}} \tan^{-1} \left[\frac{m_0}{M} \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \right] \quad (28)$$

Hence the maximum displacement (y_2) of the struck point is given by

$$y_2 = v_0 \theta \sqrt{\frac{1}{4} \frac{a}{l} \frac{m_0}{M}} \cdot e^{-\frac{M}{m_0} \cdot \frac{1}{\sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)}} \tan^{-1} \left(\sqrt{\frac{m_0}{M} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \right)} \quad (29)$$

The pressure law is obtained from equation (26) :

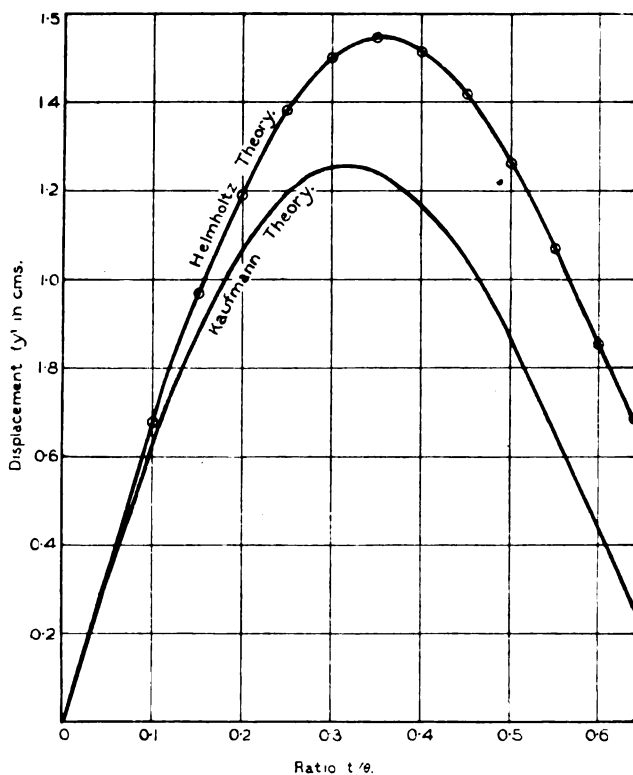
$$\begin{aligned} m_0 \frac{d^2 y}{dt^2} &= \frac{2Mv_0 e^{-\frac{M}{m_0} \cdot \frac{t}{\theta}}}{\theta \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)}} \left\{ \left(\frac{M}{m_0} - \frac{2l}{a} \right) \right. \\ &\times \sin \left[\frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \right] - \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \\ &\times \cos \left[\frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \right] \left. \right\} \quad (30) \end{aligned}$$

Finally the area between the curve and the axis of time is found from equation (23) by integrating by parts and solving for the desired integral, whence

$$\begin{aligned} \int_0^t y dt &= \frac{v_0}{\sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)}} \frac{\theta^2 a m_0}{4M} \left\{ \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \right. \\ (0 < \frac{t}{\theta} < \frac{b}{l}) &- e^{-\frac{Mt}{m_0 \theta}} \left[\frac{M}{m_0} \sin \left\{ \frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \right\} \right. \\ &+ \left. \left. \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \cos \left\{ \frac{t}{\theta} \sqrt{\frac{M}{m_0} \left(\frac{1}{4} \frac{l}{a} - \frac{M}{m_0} \right)} \right\} \right] \right\} \quad (31) \end{aligned}$$

The comparison of the theoretically and experimentally determined quantities will be given in the second part of the paper.

Fig. 2.

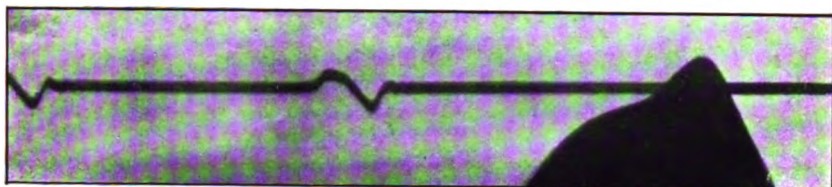


Theoretical displacement-time curves for the struck point.
 $M=29.4$; $m=49.5$; $m_0=50.6$; $\theta=1/47$; $\tau/\theta=0.64$; $v_0=325$;
 $v=-224$; $Ua=9$.

The writer wishes to thank the Council of the University College, Nottingham, and the Department of Scientific and Industrial Research for research grants; Prof. E. H. Barton, F.R.S., for his sympathetic interest in the work; Mr. F. Underwood, B.Sc., for kindly verifying the mathematics.

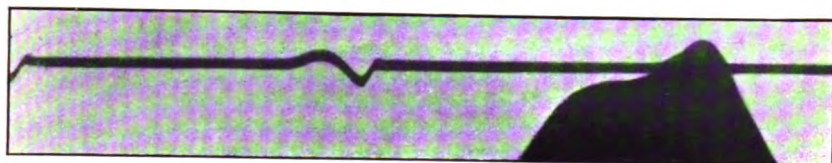
University College, Nottingham,
 Dec. 1923.

FIG. 1.



Experimental Displacement-Time Curve. Wedge-shaped metallic hammer.
 $m/M=0.27$; $l/a=26$.

FIG. 2.



Experimental Displacement-Time Curve. Broad felt-covered hammer.
 $m/M=0.27$; $l/a=26$.

FIG. 3.

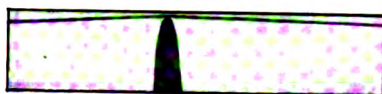


FIG. 4.



LIV. *The Potential Gradient in the Sodium-Potassium Vapour Arc Lamp.* By F. H. NEWMAN, D.Sc., A.R.C.S., Professor of Physics, University College, Exeter*.

1. *Introduction.*

A SODIUM-POTASSIUM vapour arc lamp similar in principle to the more familiar mercury vapour lamp has been previously described by the author†. This lamp works with a relatively small applied potential difference,—the arc can be struck with 30 volts,—and when once the arc has been started the fall of potential between the terminals is only 10 volts with a current of 1.5 amp. This potential difference is very small when compared with the carbon arc, and is less than that required to operate the mercury arc except the low voltage arc in mercury vapour, which acts on a different principle.

The relative intensity of the potassium and sodium lines emitted when the alloy lamp is working varies in different parts of the tube. The potassium lines are brightest near the anode. At the cathode the subordinate lines of sodium are the most intense.

The theoretical value of the resonance potential of sodium vapour is 2.10 volts, and electrons of this energy produce the D lines. Electrons having a velocity corresponding to 5.13 volts are able to ionize sodium vapour and cause it to emit all the lines, including those of the subordinate series. The resonance potential of potassium vapour is 1.60 volts, while the ionization potential is 4.33 volts. In a mixture of sodium and potassium vapours, as the accelerating potential is increased the 7699, 7665 doublet of potassium should appear first, then the 5896, 5890 doublet of sodium, followed by the subordinate series lines of potassium and sodium respectively. It would thus appear that as the potassium lines are brightest near the anode of the lamp, the fall of potential at this terminal is less than at the cathode. Low voltage arcs in metallic vapours suggest that it is possible to eject the electron to infinity from the $2p$ ring, for these arcs operate at a potential below the ionization potential. The energy necessary to eject the electron from this orbit will certainly be less than that required if the electron is in the $1.5 S$ orbit. The transfer to the $2p$ ring may be obtained by

* Communicated by the Author.

† Phil. Mag. vol. xlv. Nov. 1922.

means of the energy obtained from the bombardment by electrons having energy equal to the resonance potential, or by the absorption of radiation $h\nu$ from adjacent atoms which are in the partially ionized condition. Atoms of metallic vapours seem to permit of the radiant energy, liberated by each electron impact which results in radiation, to be passed on from atom to atom, and this multiplies the fraction of atoms which are in the abnormal or partially ionized condition. The greater part of the radiation emitted when the electrons fall from the $2p$ to the $1.5S$ ring will escape from the tube, but some of it may be taken up by neighbouring atoms. This absorption effect will increase with the vapour pressure, and with an increase in the density of the bombarding electrons. In the alloy vapour lamp the conditions are such that the ionization is produced mainly by this "cumulative action."

When the electrical discharge passes through gases at low pressure the cathode and anode falls of potential depend on the nature of the electrodes, and they fall to comparatively low values for the strongly positive alkali metals. Mey* has shown that the alloy of sodium and potassium, used as the cathode, has a smaller cathode fall in most gases than that of any metal, so it is to be expected that the potential difference between the terminals in the alloy lamp would be small.

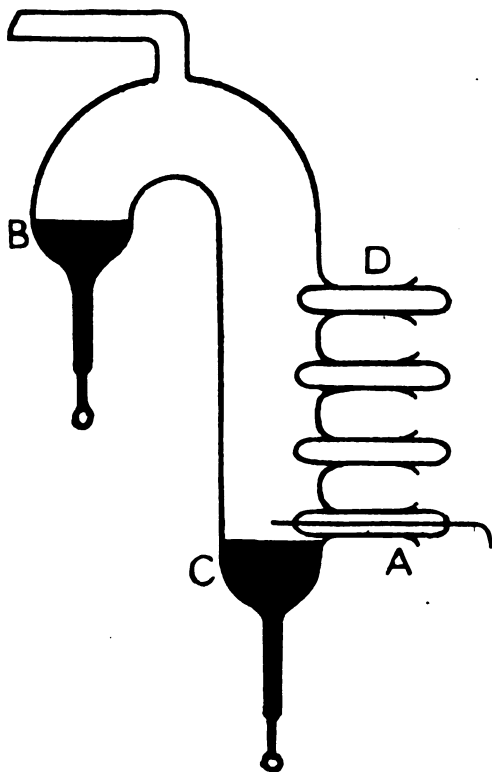
In the investigation of the distribution of electron force along the arc of the lamp the probe method was employed. The potential acquired by a platinum wire placed in various positions along the line of discharge was measured, and if it is assumed that the potential of the wire is the same as that of the vapour with which it is in contact, we get from these observations a means of determining the distribution of the electric force along the lamp. For such a method to be successful the secondary probe electrode must take up the potential of the vapour with which it is in contact. To enable it to do so there must be a plentiful supply of both positive and negative ions in the gas to give up their charges to the wire, and thus raise or lower the potential of the wire to equality with the surrounding vapour. In the arc discharge there is a copious supply of ions of both signs, so the assumption that the secondary electrode does acquire the potential of the vapour with which it is in contact seems to be justified.

* *Verh. Deutsch. Physik. Gesel.* v. p. 72 (1903).

2. Experiments.

The form of lamp used is shown in fig. 1. A quartz tube was bent to the shape shown in order that both electrodes should consist of the alloy,—two parts by weight of sodium, and one of potassium. Connexion was made with these

Fig. 1.



electrodes by aluminium wires sealed into the quartz with sealing-wax. Providing the current was not greater than 2 amps. the wax did not soften. The tube, which was about 10 cm. long and 1 cm. in diameter, had four side tubes each 3 cm. long for the insertion of the probe electrode. The latter consisted of a platinum wire sealed into a glass stopper with 3 mm. of wire protruding from the end inside the lamp.

As very little external heating is required to start the arc, the ends of these side tubes remained cool and so the vacuum was maintained. It was arranged that the platinum wire should reach the axis of the main tube. The alloy was introduced into the lamp at A, and after the apparatus had been well exhausted the surface of the alloy was made clear by passing an electrical discharge through the tube, the film of oxide disintegrating and dissolving in the alloy. By tilting the tube some of the alloy could then be run into the part B without fouling the length of the tube. The amount of alloy in C could be adjusted so that the surface was about 3 mm.—as measured by a cathetometer—from the probe electrode inserted at A. The total length measured along the axis of the lamp between the surfaces of the two alloy terminals was 8 cm.

The electrode C was connected to one pair of quadrants of a Dolezalek electrometer, and the probe electrode to the other pair of quadrants, the needle of the electrometer being maintained at 100 volts. The current through the lamp was kept constant by means of an adjustable resistance placed in series. It was found that with this shape of lamp the arc did not wander, and so the current remained constant once the temperature of the lamp reached a steady value. The arc was struck by connecting one terminal to a small induction coil and passing a momentary discharge, although sometimes the arc would strike automatically with an applied potential difference of 50 volts by slightly heating the cathode. The side tube D was situated rather more than half way along the lamp. At first C was made the cathode and the potential difference between it and the probe, inserted in the four side tubes, was determined. The current was then reversed and C was the anode. The potential difference between it and the four positions of the probe was again determined. In this way the uncertainty of obtaining correct measurements near B was avoided.

3. *Experimental Results.*

The results obtained for the potential gradient along the lamp are shown in Table I.

These results show that the potential gradient along the arc column is uniform, and therefore, as shown by Poisson's

law $\frac{\delta^2 V}{\delta x^2} = -4\pi\rho$, there cannot be a preponderance of ions of one sign or the other in it. The cathode fall—3.8 volts—is

greater than the anode fall—2·5 volts,—but both are small compared with the results for other metal electrodes.

TABLE I.

Potential difference between terminals 12·0 volts.

Current in lamp 1·5 amp.

Distance from cathode.	Corresponding Potential.	Distance from anode.	Corresponding Potential.
cathode.	0 volts.	anode.	12·0 volts.
3 mm.	3·8 „	3 mm.	9·5 „
18 „	5·0 „	18 „	8·3 „
32 „	6·1 „	32 „	7·2 „
48 „	7·4 „	48 „	5·9 „

Unfortunately the current through the lamp cannot be increased much more than 2 amp. as the heat developed causes a brown deposit on the quartz to appear, and this interferes with the steady working of the lamp. It was found, however, that for currents between 1 and 2 amp. both the cathode and anode falls of potential decreased slightly with increasing current. This is probably due to the increase in the vapour density.

The wave form of the current was investigated with Duddell's permanent magnet type of oscillograph. The vibrator was specially stretched so that it was able to follow any variation in the current up to 500 per second. The resulting curves were photographed by means of a falling plate camera, the speed of the plate at the instant of photographing being about 400 cm. per second. The vibrator, in series with a high non-inductive resistance, was placed in shunt with the main current. The resulting oscillograms were straight lines showing that the current was very steady. The potentials measured were therefore the actual potentials at the different parts of the lamp and not average potentials.

The small potential difference between the terminals of the lamp when the arc is passing depends on the photo-electric effect exhibited by the alloy. In a vacuum such as is present in the lamp, the negative corpuscles are projected

with sufficient energy to make their way against a small retarding force. The electrons near the surface of the alloy ionize the vapour, even though the electric field is so weak that the kinetic energy given by it to the electrons is too small to make them act as ionizers. Warburg* has shown that the presence of minute traces of oxygen in gases such as hydrogen or nitrogen produces a great diminution in the current from a negative point, which seems to indicate that oxygen has a great tendency to collect round the carriers of the negative charge, and either makes them less efficient as ionizers, or else makes them move more slowly in the electric field. It is probable too that oxygen increases the difficulty of getting the electrons from the point into the gas, as Warburg has shown that the presence of a trace of oxygen produces a large increase in the cathode fall of potential in vacuum tubes. All traces of oxygen are of course removed in the lamp by the sodium-potassium alloy, and this fact causes the potential gradient along the lamp to be small.

The photoelectric effect produces the same effect, although in a smaller degree, as the emission of electrons from the incandescent filament in low voltage arcs. With such arcs it is always found that the striking potential difference is always greater than that required to maintain the arc, and this is so with the alloy vapour lamp.

4. *Summary.*

1. The potential gradient along the arc of a vapour lamp using the liquid alloy of sodium and potassium as terminals has been investigated.
2. The cathode fall of potential is greater than the anode fall, but both are small compared with results for other metal terminals. The potential gradient along the arc column is uniform.
3. The small potential difference between the terminals of the lamp when it is working is explained by the photoelectric effect exhibited by the alloy.

* *Ann. der Phys.* xi. p. 295 (1900).

LV. *On the Anomalous Behaviour of a Vibration Galvanometer.* By E. V. APPLETON, M.A., D.Sc., Cavendish Laboratory, Cambridge*.

THERE is in use in the Advanced Practical Physics class at the Cavendish Laboratory a vibration galvanometer which, for quantitative work, has been found to exhibit certain peculiarities in that one of two possible deflexions is obtainable for a single value of the current passing through the galvanometer coil. The particular deflexion obtained in any case is dependent on the method by which the current is made to approach its final value. From time to time students † in the class have been asked to investigate experimentally the relation between the amplitude of oscillation of the suspended system and the frequency and amplitude of the alternating current passing through the instrument. The present paper deals with some of the results of these investigations, to which I have added an approximate theoretical treatment which seems to account for the salient features of the phenomenon.

The instrument is of the Drysdale-Tinsley type, being in principle very similar to a Kelvin Mirror-galvanometer. The vibratory system is a suspension piece carrying a light mirror, to which is attached a small magnet of soft charcoal iron, the whole being suspended between the poles of a horse-shoe magnet. The natural period of the suspended system is controlled by means of a movable magnetic shunt on the permanent magnet. The exciting current passes through a fixed coil, the plane of which is parallel to the zero position of the suspended magnet.

If the position of the magnetic shunt is kept fixed, and thus the natural frequency of the suspended system kept constant, there are three variables to be considered, namely, the oscillatory amplitude A of the galvanometer, and the magnitude and angular frequency (I and p respectively) of the alternating current through the coil. Accordingly, the characteristic relations are given by plane curves showing the variation of the amplitude A with the current I for different values of the angular frequency p , or by curves

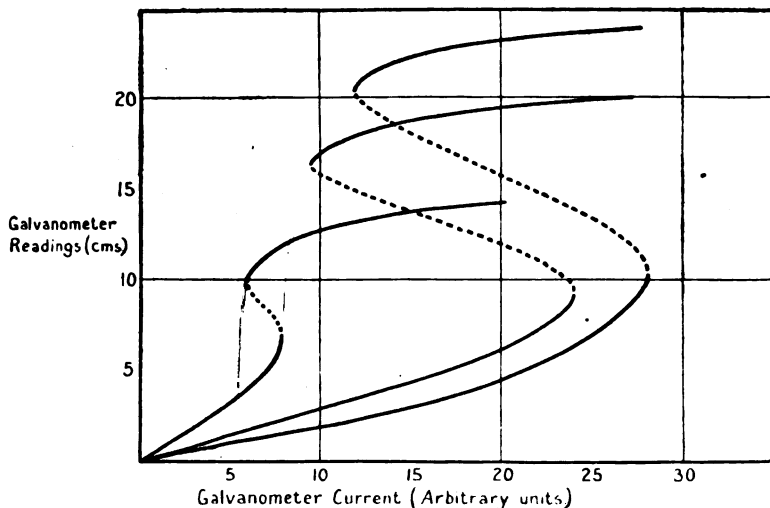
* Communicated by the Author.

† In this connexion I should like specially to mention Mr. R. W. Scholfield, of Trinity College, who was the first student to get a complete set of experimental results. His curves are reproduced in this paper.

showing the variation of amplitude with angular frequency for different values of constant current. The corresponding two sets of curves are illustrated in figures 1 and 2.

The data for the curves of fig. 1 were obtained by direct experiment, while those for fig. 2 were obtained indirectly from experimental values such as those exhibited in fig. 1.

Fig. 1.

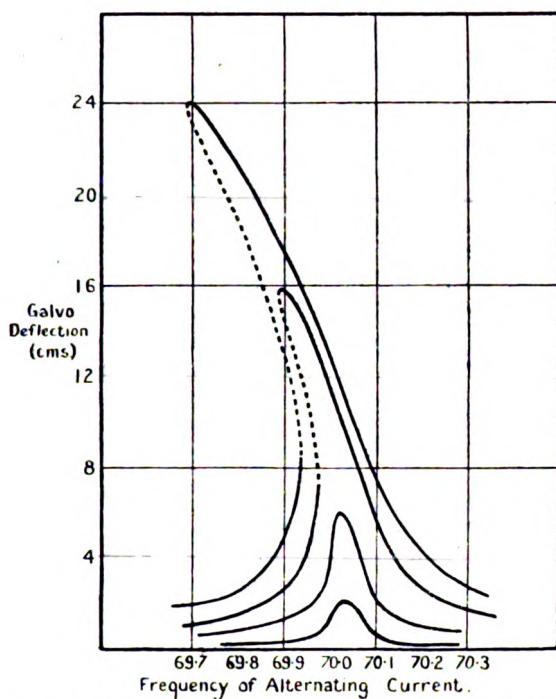


Showing relation between galvanometer current and galvanometer deflexion for different values of impressed frequency.

In obtaining the relation between the galvanometer deflexion and galvanometer current for a fixed impressed frequency cases of oscillation-hysteresis were obtained. This phenomenon is illustrated by the hysteresis loops in the curves in fig. 1. A typical example of this is redrawn in fig. 3.

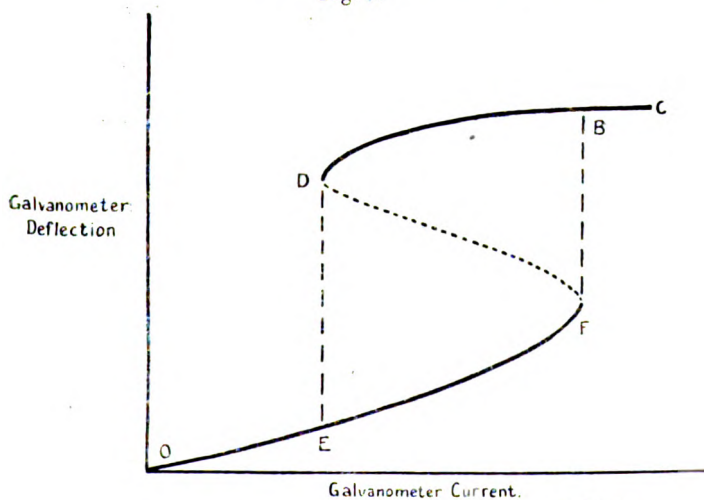
In obtaining the data for this type of curve the current in the galvanometer circuit was introduced from an alternating-current source by means of a small air-core transformer with variable coupling, so that the galvanometer-current amplitude was continuously variable. On increasing the current amplitude from zero the galvanometer deflexion increased until conditions represented by the point F were reached, when the deflexion suddenly increased to the value indicated by B. For further increase of current the representative point of the diagram moved along the curve BC. On now reducing the current, the larger deflexion indicated by BD

Fig. 2.



Showing relation between impressed frequency and galvanometer deflection for different values of galvanometer current.

Fig. 3.



was maintained, until at conditions represented by D the amplitude suddenly fell to the lower value indicated by E. In other words, when the galvanometer current was increased from zero and then decreased again, the representative point traced the path OEFBCBDEO in fig. 3.

Between the two stable values of the galvanometer amplitude indicated by EF and DB there is a kind of "threshold" amplitude indicated by the broken line DF. Its physical existence is not easily realized, but I have found the following method useful in explaining the matter to students. Let us suppose that the galvanometer is maintaining the higher amplitude indicated by a point on DB when the galvanometer circuit is opened for a moment, cutting off the current supply. The amplitude falls rapidly, but if the circuit is quickly closed again the original amplitude is finally regained. If, however, the experiment is repeated, and the circuit is kept open long enough to allow the amplitude to fall just below the critical value indicated by the appropriate point on DF, the final amplitude attained, when the current flows again, is that indicated by a point on EF. After a few trials the appropriate amplitudes for the critical "threshold" values of DF may be approximately obtained in this way.

It is obvious from the curve of fig. 3 that for the region in which oscillation-hysteresis is found there are three possible oscillatory amplitudes of the suspended system of the galvanometer for one value of the current through the coil. Two of these amplitudes (represented by DB and EF) are stable, while the intermediate value (represented by DF) is unstable. It is also clear that this phenomenon is due, in some way, to the existence of some non-linear property or properties in the galvanometer system, but it is not obvious from figs. 1 & 3 whether such non-linearity is to be assumed in the terms representing the frictional and damping forces or in the terms associated with the restitution forces. The resonance curves of fig. 2, however, immediately suggest an alteration of the natural frequency of the galvanometer system with amplitude, and one is thus led to try to explain the phenomenon as a case of forced vibrations in an oscillatory system, the restoring force of which is not proportional to the displacement. A consideration of the design of the galvanometer shows that such non-linear forces are certainly to be expected. In this connexion there are three possible effects which tend to destroy the proportionality between

restoring couple and deflexion. These may be enumerated as follows:—

- (1) The pole-strength of the soft-iron magnet will not be independent of amplitude, but will decrease with increasing amplitude. Apart from hysteresis, its magnitude will be proportional to $\cos \theta$, where θ is the angle of deflexion*.
- (2) The restoring couple, apart from the inconstancy of pole-strength, will be proportional to $\sin \theta$ and not to θ .
- (3) Since the pole-pieces of the permanent magnet are not very large, the magnetic field is most probably not homogeneous, being weaker at the sides of the gap than in the middle.

All of these effects act in the same way—that is to say, they tend to make the restoring force proportionally smaller the larger the angular deflexion. Bearing this in mind, we are at once led to suggest as a first approximation for the equation of motion of the suspension

$$K \frac{d^2\theta}{dt^2} + \left(A + \frac{B}{R} \right) \frac{d\theta}{dt} + c\theta(1 - \lambda\theta^2) = GI, \quad \dots (1)$$

where

- K is the moment of inertia of the suspended system,
 R the resistance of the galvanometer and circuit,
 c the restoring couple per unit (small) angular displacement,
 I the current through the galvanometer coil,
 t the time,

and A , B , G , and λ are constants depending on the size and dimensions of the suspension, and on the magnitude and configuration of the magnetic field. For the experiment we are considering, I is sinusoidal ($I = I_0 \sin pt$), while R is constant. We may therefore write (1) as

$$\frac{d^2\theta}{dt^2} + 2\kappa \frac{d\theta}{dt} + \omega^2\theta(1 - \lambda\theta^2) = E\omega^2 \sin pt, \quad \dots (2)$$

where

$$2\kappa = \frac{A}{K} + \frac{B}{RK}, \quad \omega^2 = \frac{c}{K}, \quad \text{and} \quad E\omega^2 = \frac{GI_0}{K}.$$

* It may here be noted that the variation of the pole-strength with amplitude will have an effect on the "frictional" terms, in that the electromagnetic damping will not be strictly proportional to the angular velocity of the system.

Equation (2) will therefore be taken as the representative differential equation of motion of the galvanometer suspension, and we now proceed with its approximate solution.

Since we are interested only in the final amplitude of the forced vibration, we may neglect the transient terms representing the free vibration and adopt as a trial solution

$$\theta = a \sin pt + b \cos pt, \quad . \quad . \quad . \quad . \quad (3)$$

where a and b are unknown functions of the time. From the physical nature of the problem we may expect the growth or decay of the amplitude to vary slowly compared with the oscillation itself. In other words, we may assume that

$$\frac{da}{dt} \ll pa$$

and

$$\frac{db}{dt} \ll pb.$$

Hence the second differential coefficients of a and b with respect to time will be neglected. We thus have

$$\frac{d\theta}{dt} = \frac{da}{dt} \sin pt + ap \cos pt + \frac{db}{dt} \cos pt - bp \sin pt, \quad . \quad (4)$$

and

$$\frac{d^2\theta}{dt^2} = 2 \frac{da}{dt} p \cos pt - ap^2 \sin pt - 2 \frac{db}{dt} p \sin pt - bp^2 \cos pt. \quad (5)$$

In considering the non-linear term involving θ^3 we may, as a first approximation, neglect the influence of the harmonics on the fundamental and retain only those terms involving the angular frequency p . We thus have

$$\theta^3 = \frac{3}{4}a^3 \sin pt + \frac{3}{4}a^2b \cos pt + \frac{3}{4}ab^2 \sin pt + \frac{3}{4}b^3 \cos pt. \quad . \quad (6)$$

On substituting for $\frac{d\theta}{dt}$, $\frac{d^2\theta}{dt^2}$, and θ^3 from (4), (5), and (6) in (2) and equating separately the terms involving $\sin pt$ and $\cos pt$, we have

$$\left. \begin{aligned} 2\kappa \frac{da}{dt} - 2p \frac{db}{dt} + a(\omega^2 - p^2) - 2\kappa pb - \frac{3}{4}\omega^2 \lambda a(a^2 + b^2) &= E\omega^2, \\ 2\kappa \frac{db}{dt} + 2p \frac{da}{dt} + b(\omega^2 - p^2) + 2\kappa pa - \frac{3}{4}\omega^2 \lambda b(a^2 + b^2) &= 0. \end{aligned} \right\} \quad . \quad . \quad . \quad (7)$$

But for stationary conditions, when a and b are constant, (7) becomes

$$\left. \begin{aligned} (\omega^2 - p^2)a - 2\kappa pb - \frac{3}{4}\omega^2\lambda a(a^2 + b^2) &= E\omega^2, \\ (\omega^2 - p^2)b + 2\kappa pa - \frac{3}{4}\omega^2\lambda b(a^2 + b^2) &= 0. \end{aligned} \right\} \quad (8)$$

Let us now make the substitutions

$$\frac{p}{\omega} = x,$$

$$\frac{\kappa}{\omega} = \alpha,$$

and

$$\frac{3}{4}\lambda = \beta.$$

In this way (8) becomes

$$\left. \begin{aligned} [1 - x^2 - \beta(a^2 + b^2)]a - 2\alpha xb &= E, \\ [1 - x^2 - \beta(a^2 + b^2)]b + 2\alpha xa &= 0. \end{aligned} \right\} \quad (9)$$

Let us further write

$$y = a^2 + b^2,$$

where y is the square of the amplitude A for stationary conditions. In this way (9) becomes

$$(1 - x^2 - \beta y)^2 y + 4\alpha^2 x^2 y = E^2, \quad (10)$$

a cubic equation in y , the real roots of which give us the values of the possible stationary amplitudes.

But the possible amplitudes are not necessarily stable. We must therefore determine the criteria of stability for each solution. In determining such criteria we may follow the ordinary methods of dynamics and, in considering the effect of a small change of amplitude due to some disturbing cause, investigate whether the amplitude tends to return to or depart further from its initial stationary value. Thus, let us suppose that the oscillatory system is disturbed so that a becomes $a + \Delta a$ and b becomes $b + \Delta b$, where Δa and Δb are small. On making these substitutions in (7) and neglecting squares of small quantities, we have

$$\left. \begin{aligned} [2\alpha D + (1 - x^2) - 3\beta a^2 - \beta b^2]\Delta a \\ \quad + [-2\alpha D - 2\alpha x - 2\beta ab]\Delta b = 0, \\ [2\alpha D + 2\alpha x - 2\beta ab]\Delta a \\ \quad + [2\alpha D + (1 - x^2) - \beta a^2 - 3\beta b^2]\Delta b = 0, \end{aligned} \right\} \quad (11)$$

where D has been written for $\frac{1}{\omega} \frac{d}{dt}$. Assuming $\Delta a = F e^{mt}$

and $\Delta b = Ge^{mt}$, we obtain a quadratic equation for m , namely,

$$Am^2 + Bm + C = 0, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where

$$A = 4\alpha^2 + 4x^2,$$

$$B = 4\alpha(1 + x^2 - 2\beta y),$$

and

$$C = (1 - x^2)^2 + 4\alpha^2 x^2 - 4\beta y(1 - x^2) + 3\beta^2 y^2.$$

Now, for the amplitudes a and b to be stable, the roots of the equation for m must have a negative real part. Thus for stability we must have

$$\left. \begin{array}{l} A > 0, \\ B > 0, \\ \text{and } C > 0. \end{array} \right\} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

It is obvious that the first of these conditions is always satisfied, and it will be shown later that the second is always satisfied for the experimental conditions we are considering. But the third condition is sometimes not fulfilled for normal experimental conditions, indicating cases of possible but unstable amplitudes.

In elucidating the various facts concerning the possible amplitudes and their stability, we shall find it convenient to think in terms of the ordinary resonance curve as exemplified in fig. 2. The variables x and y have been so chosen that the relation (10) plotted in the ordinary way gives us theoretical curves of this type. Before plotting such curves, however, we may consider the value of the tangent $\frac{dy}{dx}$ at various points. On differentiating (10) with respect to x , we have

$$\frac{dy}{dx} = \frac{4xy(1 - x^2 - 2\alpha^2 - \beta y)}{(1 - x^2)^2 + 4\alpha^2 x^2 - 4\beta y(1 - x^2) + 3\beta^2 y^2},$$

or

$$\frac{dy}{dx} = \frac{D}{C},$$

where

$$D = 4xy(1 - x^2 - 2\alpha^2 - \beta y),$$

and, as previously,

$$C = (1 - x^2)^2 + 4\alpha^2 x^2 - 4\beta y(1 - x^2) + 3\beta^2 y^2.$$

We may further note that $C = 3C_1C_2$, where

$$C_1 = \frac{2}{3}(1-x^2) + \frac{1}{3}(1-x^2)\sqrt{1 - \frac{12\alpha^2 x^2}{(1-x^2)^2} - \beta y},$$

and

$$C_2 = \frac{2}{3}(1-x^2) - \frac{1}{3}(1-x^2)\sqrt{1 - \frac{12\alpha^2 x^2}{(1-x^2)^2} - \beta y}.$$

Thus for the series of resonance curves mentioned above, the following general summary may be made :—

- (a) The tangents of the resonance curves are horizontal for points on the curve $D=0$.
- (b) The tangents of the curves are vertical at points on the two curves $C_1=0$ and $C_2=0$.
- (c) An amplitude value is stable only when $C>0$ and $B>0$.

These points may further be illustrated by fig. 4, in which the curves $D=0$, $C_1=0$, $C_2=0$, and $B=0$ are drawn for the resonance region, where x is approximately equal to unity.

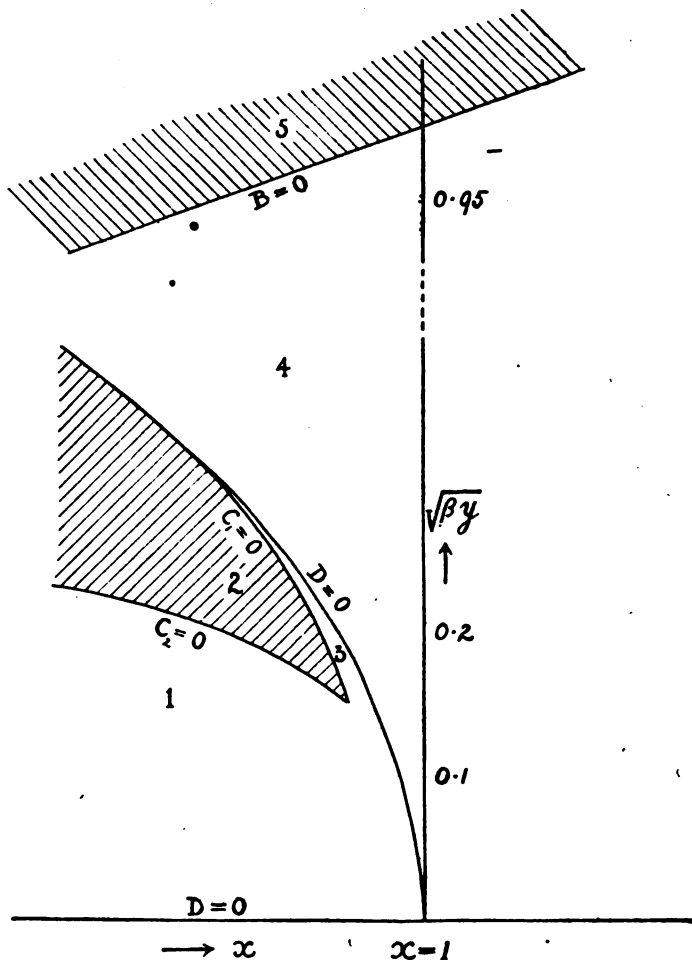
The values of the ordinates for the curve $B=0$ are much larger than the corresponding ordinates of the other curves. This is indicated by the break in the axis of $\sqrt{\beta y}$. With the aid of this diagram we may examine the stability of the various solutions. In doing this it is convenient to divide the diagram into regions, as numbered in the figure, and tabulate the data as follows :—

Region.	D.	C_1 .	C_2 .	C.	B.	Nature of Oscillation.	$\frac{dy}{dx}$.
1	+	+	+	+	+	Stable.	+
2	+	+	—	—	+	Unstable.	—
3	+	—	—	+	+	Stable.	+
4	—	—	—	+	+	Stable.	—
5	—	—	—	+	—	Unstable.	—

The regions of instability indicated by this table have been

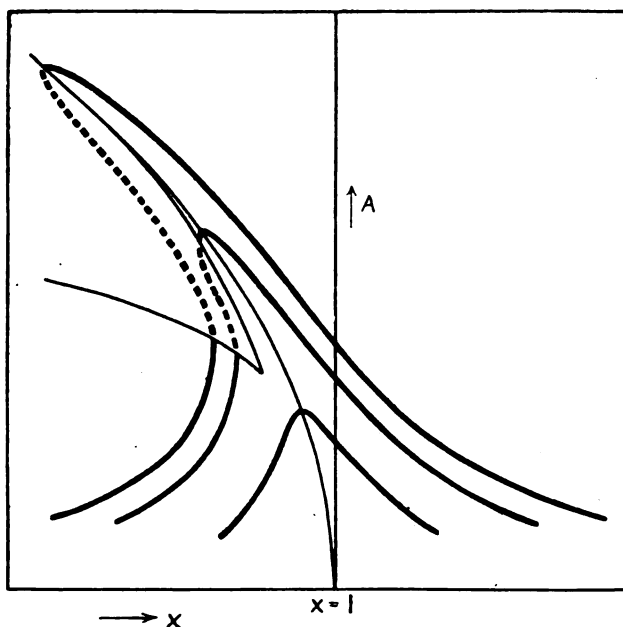
shown shaded in fig. 4. The unstable region above the curve $B=0$ is never reached in actual practice.

Fig. 4.



A complete series of theoretical resonance curves are shown in fig. 5. These were drawn using equation (10). The points of horizontal tangent ($D=0$) and the points of vertical tangent ($C=0$) are also shown. In accordance with the results of the table the amplitudes indicated by the dotted lines are unstable.

Fig. 5.



Showing theoretical resonance-curves.

It will be seen that the theoretical curves of this figure are of a type similar to the experimental curves shown in fig. 2.

Cambridge, August 1923.

(Note.—While this paper was in course of communication, a paper by F. Waibel appeared in the *Annalen der Physik*, lxxii. p. 3, no. 19 (1923), in which a case of oscillation-hysteresis in a vibration-galvanometer is recorded, but no theory of the behaviour is given.)

LVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 480.]

January 9th, 1924.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair

THE following communications were read :—

1. 'The Geological Structure of the Clevedon-Portishead Area (Somerset).' By Prof. Sidney Hugh Reynolds, M.A., Sc.D., F.G.S., and Edward Greenly, D.Sc., F.G.S.

The area described is, in the main, a prominent ridge some 4 miles long, forming the extreme north-western portion of Somerset

and extending between the small towns of Clevedon and Portishead. It is one of a number of similar ridges in Northern Somerset composed of Carboniferous Limestone alone, or of Carboniferous Limestone and Old Red Sandstone, but differs from all the others in that it trends north-east and south-west, instead of east and west.

The main part of this ridge is of very simple structure, consisting of Old Red Sandstone overlain by Carboniferous Limestone (K, Z, and C beds) dipping south-eastwards at an angle which averages about 35° to 40° . These rocks form the north-western limb of a synclinal fold, the south-eastern limb of which is seen only in a series of isolated exposures at Clevedon, at Weston Big Wood, and at Portishead. At Weston Big Wood, where the rocks of the south-eastern limb are vertical or slightly overfolded, nothing below Z_2 is seen; but at Portishead a south-westerly pitch in the axis of the fold brings the lowest Carboniferous and Old Red Sandstone to the surface, the rocks being (as at Weston Big Wood) usually vertical or slightly overfolded. At the Clevedon end the infold pitches north-eastwards, and beds as high as the Coal Measures are involved.

The folding along the dominant north-east and south-west axis was accompanied by overthrusting from the south-east, which caused *Caninia* Oolite (C_1) to be driven over the Coal Measures and the Z beds over the *Caninia* Oolite at Bella Vista, Clevedon: while Dial Hill, Clevedon, consists of an overthrust outlier of steeply inclined C beds resting partly on C beds, but mainly on Z beds, and Fore Hill, Portishead, one of gently dipping Z beds resting upon vertical Old Red Sandstone. At both ends of the area there are further complications, leading in each case to a partial resumption of the east-and-west strike.

At Portishead the transverse disturbance seems to take the form of a northward thrusting of the main body of the ridge over the east-and-west striking rocks of the Eastwood Ridge.

At the Clevedon end the transverse disturbance has also the form of a northward overthrust, the members of the north-east and south-west series being again driven over the east-and-west series; but here one of the major thrust-planes of the north-east and south-west series appears to be involved in the disturbance, and doubled back on itself at the Hill Road Crag, Clevedon.

2. 'The Avonian of the Tytherington-Tortworth-Wickwar Ridge (Gloucestershire).' By Frederick Stretton Wallis, Ph.D., F.G.S.

The author describes and maps, in terms of Vaughan's system of zonal nomenclature, the northern portion of the horseshoe-shaped ridge of Avonian rocks which partly surrounds the synclinal basin of the Bristol Coalfield. The chief points of interest may be summarized as follows:—

- (1) The recognition of all zones, with the exception of the *Dibunophyllum* Zone.

- (2) The great expansion and fossiliferous character of the 'Sub-Oolite' bed as compared with that exhibited in the type-section of the Avon.
- (3) The early incoming of 'Millstone Grit' conditions at the top of S_2 adds a further link to the accumulated evidence regarding the entrance of this sandy phase at progressively lower horizons north of Bristol.

3. 'The Avonian of the Western Mendips, from the Cheddar-Valley Railway to the Sea, west of Bream Down.' By Miss Agnes Elizabeth Bamber, M.Sc.

Comparison is made between the Avonian of the Western Mendips, and (a) the Avon section and (b) the Burrington Combe section. The outcrops of the Carboniferous Limestone zones have been mapped, the zonal notation of the late Dr. Vaughan being utilized. Levels from K_2 to S_1 are exposed in the area. The lithological and paleontological characters are described.

The usefulness of the application of Vaughan's zonal notation to Carboniferous Limestone outside the Bristol area has been again proved. The conclusions arrived at by Principal T. F. Sibly, and stated in his Mendip paper, have been confirmed. With the exception of the C_2 to S_1 beds, the lithological sequence in the Western Mendips is essentially similar to that of the Avon section. *Modiola*-phase conditions in S_1 extended to the Western Mendips, but were not completely established there. The divergence from C_2 - S_1 conditions of the Avon section is slightly less in the Western Mendips than at Burrington. K_2 , β , and Z_1 , hitherto unrecorded from the area, are exposed. *Conocardium* sp. and *Spiriferina* (probably an early form of *insculpta*) have been recorded from low in γ , and *Cyathophyllum* θ from the lowest beds of C_1 .

January 23rd.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

The following communication was read:—

'On a Recently Discovered Breccia-Bed underlying Nechells (Birmingham), and its Relations to the Red Rocks of the District.' By Prof. William S. Boulton, D.Sc., F.G.S.

A recent boring for water at Nechells Gasworks (Birmingham) has revealed an unexpected succession of rocks, which appear to have an important bearing on the problem of the 'Permian' of the Midlands and its relation to the Carboniferous and Trias.

The cores from the boring are described in detail, and it is shown that here the Keuper Sandstone (272 feet thick) rests unconformably upon a coarse breccia (Nechells Breccia) 350 feet thick, which in turn rests unconformably on Hamstead Beds (Calcareous Conglomerate Group).

The Breccia consists of angular fragments and lumps, up to a foot or more across, derived for the greater part from Cambrian quartzite and sandy limestone with some decomposed volcanic rocks; and in the lower portion, the fragments are calcareous

sandstone of the type of the underlying Hamstead Beds. Thin beds of marl and sandstone are interbedded with the Breccia.

Fossils, belonging to the horizon just below the *Olenellus* Limestone at Comley (Shropshire) and to the horizon of the *Hyolithus* Beds at the top of the Hartshill Quartzite of Nuneaton, have been collected from lumps of the sandy limestone in the Breccia.

The extension of the Nechells Breccia underneath other parts of the Birmingham area is discussed, and evidence is adduced to show that the Bunter Beds on the west of Nechells thin out against the rising bank of Breccia; also that the Nechells Breccia was derived from an old land-surface very near Birmingham, probably on the south-east.

The relations of the Nechells Breccia to those of Hopwas and Clent are then dealt with, and evidence put forward for an unconformity at the base of the Clent Breccia. The foregoing are grouped with the Leicestershire Breccias described by Dr. H. T. Brown in 1889, with the Polesworth Breccia of North Warwickshire, and with that found in the Burcot Boring near Bromsgrove.

Thus breccias occur at intervals in a belt 40 miles long from north-east to south-west, all, so far as known, unconformable to the beds below them, and to the Trias above. Generally speaking, the material of these breccias was derived from rocks which increase in age from north to south.

The correlation of the marls with fine breccias in the Warley area, 3 to 4 miles west of Birmingham (which are apparently conformable to the Calcareous Conglomerate Group below, and were regarded by Mr. Wickham King in 1899 as the equivalent of the Clent Breccia on the south), is left in doubt until such further evidence is discovered as will show whether they are older than the Clent Breccias, and not separated from the underlying beds by a time-break; or whether they represent deposits in water-basins contemporaneous with the accumulation of the Clent Breccias.

The Breccia Group (Manor House and Tower Hill sub-groups of Mr. W. H. Hardaker), in the Hamstead Quarry Series, described by him in 1912, is shown not to exist as such, but to be part of the Calcareous Conglomerate Group.

Instances are given of Midland breccias of Triassic age, and the difficulty of discriminating in some cases between original Permian breccias and basement Triassic deposits made up of their derived material is considered.

The classification of the pre-Triassic Red Rocks of the Midlands recently adopted by the Geological Survey is discussed, and the following grouping is suggested :—

- (3) Clent Beds (Breccias of Clent, Northfield, Nechells, Hopwas, etc.).
(Unconformity)
- (2) Corley Beds (the Calcareous Conglomerate Group, with, in the meantime, the Warley and Kingswinford Marls and intercalated fine breccias of South Staffordshire, and the Tile Hill Marls and Sandstones of Warwickshire).
- (1) Keele Beds.

The age of the Corley Beds, which follow conformably upon the Keele, is still uncertain, and may eventually prove to be Permian; but the author agrees with the Geological Survey that (for the present) it is convenient to group them with the Carboniferous. The evidence now brought forward points unmistakably to the Permian age of the Clent Beds, in which the Nechells Breccia is included.

February 6th.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

The following communication was read:—

‘The Upper Towy Drainage-System.’ By Prof. Owen Thomas Jones, M.A., D.Sc., F.G.S.

The paper gives an account of the physical and main geological features of the upper part of the Towy drainage-system. The floors of the Towy valley and of its principal tributaries (the Camddwr and Pysgotwr) were levelled, in order to obtain data for constructing their longitudinal profiles. A few levels were also determined in the upper valley of the Cothi, which formerly entered the Towy valley many miles above its present mouth.

The Towy valley, for about 8 miles from the source, is fairly wide, and the opposing spurs, which usually are gently convex, are set well apart; the longitudinal profile is concave, and the lower ends of the tributary valleys are graded with the main valley. The features are those of a fully mature drainage-system. Above Fanog (8½ miles) the floor of the valley is trenched by a narrow ravine, which develops into a deep glen gradually widening downstream. Between Rhandirmwyn (15 miles) and Llandovery (22 miles) the valley presents once more a mature appearance, which it retains as far as its mouth (56 miles) below Carmarthen. The whole longitudinal profile thus consists of two concave portions, in each of which the gradient diminishes progressively downstream, separated by a short stretch with high and irregular gradient.

The upper part of the valley is attributed to a former period of base-levelling. This was followed by a rejuvenation of the drainage-system due to an uplift of the area. The present valley between Rhandirmwyn and the mouth was eroded in consequence of that rejuvenation, and is base-levelled or graded in relation to the existing sea-level. The upper or Fanog base-level, as it is termed, to which the upper part of the valley conforms, now stands much above the present sea-level. A formula was sought and found to which the profile above Fanog conforms; also the height of the Fanog base-level at the present mouth of the Towy was determined by calculation from the formula, and by comparison with the profile and gradient of the valley below Llandovery. These determinations show a difference of approximately 400 feet between the former and the existing base-levels.

The tributary valleys afford confirmation of the results obtained in the main valley. About half a mile above Nant Stalwyn

(5 miles) there is a well-marked drop or step in the rock-floor of the Towy valley. Below this step the tributary valleys hang above the main valley-floor, the discordance increasing downstream. The association of a rock-step with hanging valleys below is often regarded as evidence of Glacial erosion with overdeepening of the main valley: but, in this locality, there is conclusive evidence that the hanging tributaries are pre-Glacial. The most probable explanation of these features is that they are due to a still earlier uplift of the region, followed by rejuvenation of the valley up to the rock-step. This suggestion is borne out by the features of the tributary valleys for many miles downstream.

The part of the valley above the rock-step was, therefore, eroded in relation to a base-level older than the Fanog base-level. This, which is termed the Nant Stalwyn base-level, is estimated to stand at present nearly 600 feet above the level of the sea.

The investigation has also thrown light on past changes in the drainage-system, and may ultimately help to solve the problem of the age and origin of the great plateau of Central Wales.

LVII. Intelligence and Miscellaneous Articles.

INCREASE OF INERTIA OF BODIES VIBRATING IN A LIQUID.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the December number of the *Philosophical Magazine* there appears a note by N. C. Krishnaiyar, M.A., on the "Increase of Inertia of Bodies Vibrating in a Liquid."

His paper deals only with experiments on the increase of inertia of a sphere; and I think it may be of interest to mention some approximate values that I have been able to obtain experimentally for the increase of inertia of a marine propeller vibrating under water. The experiments have been carried out in two ways:— (1) By obtaining a curve of the amplitude of a forced vibration, and so determining the natural frequency of the system of engine, shafting, and propeller: the inertia of all other parts being known, it is easy to calculate the propeller inertia. (2) If a forced vibration is caused by the engine, the propeller inertia may be determined from the position of the node of forced vibration.

Experiments on the above lines have shown that the value of the inertia factor varies, with different shapes of propeller blade, from 2 to about 4. A knowledge of the value of the inertia factor is, of course, necessary before a calculation can be made of the natural frequency of torsional vibration of a marine-engine shafting; and with this object in view, I hope shortly to be able to carry out further experiments on the influence of the shape of a body on its inertia factor when vibrating in water.

9 Bentineck Crescent,
Newcastle-on-Tyne,
Dec. 19, 1923.

Yours faithfully,

JAMES CALDERWOOD.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

APRIL 1924.

LVIII. *Valve-generated Oscillations in Coupled Circuits.* By
E. TAYLOR JONES, D.Sc., F.Inst.P., Professor of Physics
in the University College of North Wales, Bangor*.

[Plate IV.]

1. **T**HE present paper is mainly concerned with certain phenomena which occur when a high-tension transformer, an induction coil, or other coupled system in which the secondary circuit possesses considerable electrostatic capacity, is switched into a circuit in which oscillations of audible frequency are generated by a triode valve.

The diagram in fig. 1 shows one of the arrangements of apparatus employed in the experiments. A and B are the generating coils, connected in the anode and grid circuits respectively, C_1 is the primary condenser, O_1 a current oscillograph, H a hot wire ammeter, T the transformer† or induction coil which may be shortcircuited by the key K. O_2 is an electrostatic oscillograph connected with the secondary terminals of the transformer. The deflexion shown by O_1 is proportional to the current flowing through the instrument, that of O_2 to the square of the difference of potential at its terminals. In most of the experiments four 15-watt transmitting valves were used in parallel, with anode voltage

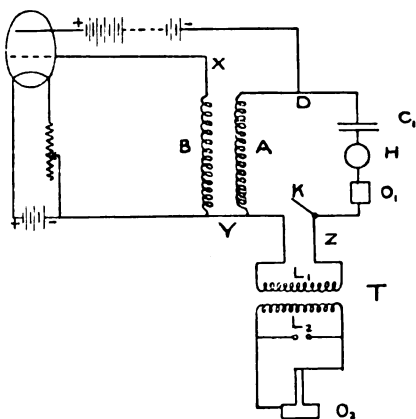
* Communicated by the Author.

† The high-tension transformer used in these experiments was kindly supplied by the Cox-Cavendish Electrical Company.

400, the anode current ranging up to 100 milliamperes. The shortcircuiting key K consisted of a mercury dipper interrupter actuated by the rotating mirror used with the oscillographs.

The oscillatory system thus consists of two coupled circuits of which the primary includes the coil A , the condenser C_1 , the ammeter and oscillograph O_1 , and the primary coil of the transformer. The capacity in the secondary circuit includes that of the oscillograph O_2 and spark-gap electrodes, and the distributed capacity of the coil, and may be increased by the addition of a variable condenser connected

Fig. 1.



to the secondary terminals. This system possesses two frequencies of oscillation which depend upon the inductances and capacities and upon the coupling of the two circuits. The coupling is less than that of the transformer alone in the ratio of L_1 , the self-inductance of the primary coil, to $L_1 + L_A$, the total self-inductance in the primary circuit. Instead of the connexions shown in fig. 1 the condenser and transformer, with the ammeter and oscillograph, may be connected between the points D and X , in which case the coupling is further reduced owing to the addition of the coil B to the primary circuit.

The oscillation may be rendered audible by means of a telephone connected with a loop of wire loosely coupled with coil A .

The following are the effects which we shall consider:—

1. When the system is oscillating with the transformer in circuit one note only is usually heard in the telephone, not two notes simultaneously as might be expected. A similar effect is also observed in other coupled systems, electrical and mechanical (*e. g.* the singing arc with coupled circuits, and reed pipes), which are maintained in oscillation, but as far as the writer is aware this effect has not hitherto been satisfactorily explained*.
2. If the system is oscillating with the key K closed and the transformer is then thrown into the circuit, the pitch of the telephone note may rise, or fall, or it may undergo no change. These various results may be produced by suitably adjusting the capacity of the condenser C_1 .
3. In the secondary circuit the potential produced at unshortcircuiting is generally much higher than that generated afterwards by the alternating current flowing in the transformer. In fact the valve may be unable to maintain any oscillation with the transformer in circuit (as for instance when the capacity C_1 is too great), and there may still be a high potential generated at the secondary terminals when the transformer is switched in.

Some of these effects are illustrated by the current oscillograms reproduced in figs. 2-8 (Pl. IV.). Fig. 2 is a typical curve showing the effect of throwing the transformer into circuit. In this case the pitch rose by about a major third at unshortcircuiting, and the sound was at the same time reduced in intensity as is indicated by the small amplitude of the maintained oscillations in the latter part of the curve†. Fig. 3 shows a similar effect but with a greater rise of pitch (in this case a minor sixth) at the introduction of the transformer. In

* A similar preference for one or other of the two vibrations of a coupled system may also be observed in the case of damped vibrations. This has been considered by M. Wien (*Ann. der Physik*, lxi. p. 162, 1897) from the point of view of the difference of the damping coefficients of the two component vibrations. In some respects, however, Wien's conclusions with regard to the damping are not in agreement with those arrived at later by Drude (*Ann. der Physik*, xiii. p. 512, 1904). Wien does not consider the case of maintained vibrations.

† The movement in all the oscillograms is from right to left. The lower curve indicates time intervals, each wave representing 1/768 second.

these two cases no spark appeared at the secondary terminals either at unshortcircuiting or afterwards. If the gap is reduced so as to allow a spark to appear at unshortcircuiting the amplitude of the curve falls much more rapidly to a smaller value, and afterwards declines slowly to its final value, as shown in fig. 4 (8.3 mm. spark). With a shorter gap (3.4 mm.) the final steady state is reached sooner, the shorter spark evidently taking more energy from the system (fig. 5). If the gap is still further reduced (or the current increased) so that sparking takes place freely under the maintained alternating current flowing in the transformer, the curve is as shown in fig. 6. It appears that each spark has the effect of reducing the amplitude of the oscillation, and that some time is required for it to recover and grow again to the value needed for a repetition of the discharge.

If the oscillograph, instead of being in the condenser circuit, is connected in the transformer primary circuit, as at Z (fig. 1), the instrument will of course show only the current flowing after the key K is opened (fig. 7).

The curve of fig. 8 was taken with an induction coil substituted for the transformer. On this occasion the condenser C_1 (2.63 mfd.) with the induction coil and oscillograph were connected between D and X (fig. 1). The curve indicates a fall of pitch of about a semitone at unshortcircuiting. Fig. 9 (Pl. IV.) shows the beginning of a train of oscillations (condenser, coil, and oscillograph between D and Y as in fig. 1) produced by closing a contact maker in the grid circuit.

It will be seen that all these curves show a single oscillation of increasing, diminishing, or constant amplitude when the transformer or induction coil is in circuit and not sparking, and that there is no evidence of a periodic fluctuation of amplitude such as might be expected in a system possessing two frequencies of oscillation.

We will now proceed to consider the reasons for the peculiar changes of pitch at unshortcircuiting, and for the almost complete absence of any trace of one or other of the two component oscillations of the system, both in the telephone sound and in the current oscillograph curves.

2. *The Apparent Self-Inductance and Resistance of the Primary Coil of a Transformer.*

In the first place it is necessary to consider certain points in the theory of the transformer regarded as a coupled system having electrostatic capacity in the secondary circuit,

to the primary of which an alternating potential of given frequency and constant amplitude is applied. Since the secondary capacity is in part distributed over the coil, and in consequence the current in the secondary wire varies along its length, we shall (after Drude *) employ a symbol (i_2) to represent the current in the central winding of the secondary coil, and shall denote by L_{21} the coefficient of induction of the primary on the secondary, by L_{12} that of the secondary on the primary. The E.M.F. applied to the primary terminals having frequency $p/2\pi$ and amplitude E , the equations for the primary and secondary currents are

$$L_1 \frac{di_1}{dt} + L_{12} \frac{di_2}{dt} + R_1 i_1 = E e^{ipt}, \quad . \quad . \quad . \quad (1)$$

$$L_2 \frac{di_2}{dt} + L_{21} \frac{di_1}{dt} + R_2 i_2 + V_2 = 0, \quad . \quad . \quad . \quad (2)$$

where V_2 is the potential at the secondary terminals. Also, if C_2 is the secondary capacity,

$$i_2 = C_2 \frac{dV_2}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Assuming that in the forced oscillation i_1 and i_2 vary as e^{ipt} , and eliminating i_2 and V_2 , we arrive after reduction at the equation for i_1 ,

$$L \frac{di_1}{dt} + R i_1 = E e^{ipt}, \quad . \quad . \quad . \quad . \quad (4)$$

where

$$L = L_1 + \frac{L_{21} L_{12} p^2 C_2 (1 - p^2 L_2 C_2)}{(1 - p^2 L_2 C_2)^2 + R_2^2 C_2^2 p^2} \dagger, \quad . \quad . \quad (5)$$

$$R = R_1 + \frac{L_{21} L_{12} p^4 C_2^2 R_2}{(1 - p^2 L_2 C_2)^2 + R_2^2 C_2^2 p^2} \dagger. \quad . \quad . \quad (6)$$

Introducing the coupling of the transformer k^2 ($= L_{21} L_{12} / L_1 L_2$), and denoting $p^2 L_2 C_2$, the ratio of the squares of the applied frequency and the natural frequency of the secondary circuit when oscillating alone, by f , and

* *Ann. d. Physik*, xiii. p. 517 (1904).

† These expressions may be deduced from those given in Professor Gray's 'Absolute Measurements in Electricity and Magnetism,' pp. 251, 252 (1921), for the more general case in which there is capacity in both primary and secondary circuits.

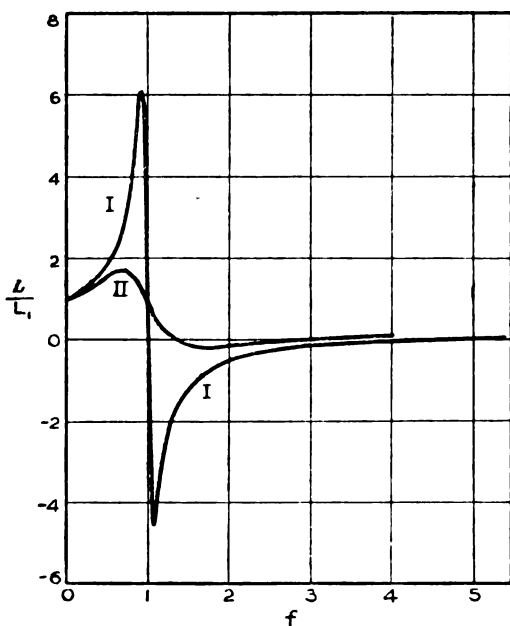
the quantity $\left(\frac{R_2}{L_2}\right)^2 L_2 C_2$ by λ , we find for L and R the expressions

$$L = L_1 \left[1 + \frac{k^2 f'(1-f')}{(1-f')^2 + \lambda f'} \right], \dots (7)$$

$$R = R_1 \left[1 + \frac{k^2 \frac{L_1}{R_1} \frac{R_2}{L_2} f'^2}{(1-f')^2 + \lambda f'} \right]. \dots (8)$$

L and R may be called respectively the "apparent self-inductance" and the "apparent resistance" of the primary coil of the transformer. They are the self-inductance and

Fig. 10.



resistance which a single coil would require to have in order to allow, under the action of the applied E.M.F. $E \cos pt$, a current i_1 to pass identical in amplitude and phase with the primary current of the transformer. The apparent impedance of the primary coil is $\sqrt{k^2 + L^2 p^2}$, and the angle by which the primary current is behind the applied E.M.F. in phase is $\tan^{-1} Lp/R$.

It appears from the expression (7) that L is equal to L_1

when the applied E.M.F. is varying infinitely slowly ($f=0$), and again in the case of resonance ($f=1$). For infinitely rapid variations ($f=\infty$) L is equal to $L_1(1-k^2)$.

The manner of variation of L with the applied frequency may be illustrated by a numerical case. For the induction coil used in the present experiments the coupling k^2 was 0.768, and in certain circumstances λ was 0.005147. These values being assumed, the variation of the ratio L/L_1 with f is shown in fig. 10, curve I. It will be seen from this curve that as the applied frequency increases from zero, L/L_1 increases from unity to a maximum of 6.16 at $f=0.93$, then rapidly diminishes and becomes zero at a value of f slightly greater than unity (1.00676). Between this value of f and 4.281, L is negative, the greatest negative value being $4.547 L_1$ at $f=1.08$. With further increase of f , L/L_1 becomes and remains positive, slowly approaching its final value 0.232.

The form of the curve in the neighbourhood of the resonance point ($f=1$) depends greatly upon the value of the coefficient λ , which is proportional to the square of the resistance of the secondary circuit. If R_2 be regarded as the effective resistance of the secondary, as determined from the damping of its oscillation when the primary is on open circuit, the value of λ may vary considerably with the conditions of the experiment. Curve II. in fig. 10 shows the variation of L/L_1 when λ is 0.174, a value determined for the same induction coil in different circumstances. In this case L is negative between the values 1.338 and 3.222 of f , but the variation of L is now much smaller and more gradual near the resonance point. The greatest positive value of L/L_1 is 1.761 at $f=0.7$, the greatest negative value 0.163 at $f=1.7$. The effect of increasing the resistance of the secondary circuit is to diminish the range of variation of L , and also to diminish the range of frequencies over which L is negative.

If λ is increased beyond a certain point the L/L_1 curve fails to intersect the horizontal axis, and L can no longer have negative values. The limiting value of λ may be found by equating to zero the expression for L given in (7). The coupling k^2 being always less than unity, the conditions that the equation for f should have real positive roots are

$$(\lambda + k^2)^2 \leq 4\lambda \quad \dots \dots \dots (9)$$

$$\text{and} \quad \lambda + k^2 < 2. \quad \dots \dots \dots (10)$$

The greatest value of λ that satisfies these conditions is

$$\lambda = 2 - k^2 - 2\sqrt{1 - k^2}. \quad \dots \dots \dots (11)$$

With $k^2=0.768$, this gives 0.2686 as the greatest value of λ which allows L to become zero. At this value of λ the L/I_1 curve touches the horizontal axis at the point

$$f = 1 / \sqrt{1 - k^2}.$$

If the resistance of the secondary circuit is so small that λ is negligible the expression (7) reduces to

$$L = I_1 \left(1 + \frac{k^2 f}{1 - f} \right), \dots \dots \dots (12)$$

which becomes infinite with change of sign at the resonance point, and changes sign again at $f=1/(1-k^2)$.

According to (7) the effect of an increase of the coupling is in general to increase the variation of L , and also to increase the range of frequencies over which L is negative. By (11) it also increases the maximum value of λ which allows L to change sign.

In the valve experiment the rise of pitch sometimes heard in the telephone when the transformer is unshortcircuited is accounted for by the fact that the apparent self-inductance of the transformer primary is negative at certain frequencies. If the frequency with the transformer in circuit lies within the range over which L is negative the frequency will increase because of the diminution of self-inductance of the whole oscillatory circuit when the transformer is introduced.

In one experiment, in which the connexions were as in fig. 1, the pitch of the note was observed to fall slightly (L positive) when the induction coil was switched in if the capacity C_1 was less than about 0.19 mfd.; at this value the pitch was the same whether the coil was in circuit or not, indicating that L was zero. If C_1 was between 0.19 and 0.902 mfd. the pitch rose at unshortcircuiting (L negative), the rise of pitch at the latter value being about a semitone. The self-inductance of coil A in this experiment was 0.086 henry, so that a rise of pitch of a semitone indicates the addition to the circuit of a self-inductance of about -0.01 henry. When C_1 was further slightly increased the pitch fell at the introduction of the coil by about the same interval, indicating a positive value for L , but it was noticed that the diminution of intensity of the sound at unshortcircuiting was considerably greater now than when L was negative. The current flowing in the oscillatory circuit was therefore considerably reduced in these circumstances, that is, just after L changed from a negative to a positive

value *. At still greater values of C_1 a fall of pitch similar in amount was heard when the coil was thrown into circuit.

If C_1 is increased from a small value with the induction coil always in circuit, the pitch falls gradually until a certain stage is reached at which a fall of a full tone occurs very rapidly. With about 0.9 mfd. in circuit this fall of pitch can be produced by as small a change as 0.002 mfd. in the value of C_1 . With further increase of C_1 the pitch gradually falls. The experiment may be varied by first adjusting C_1 nearly to the critical value, when a slight change of the filament current produces the sudden change of pitch. A change in the filament current alters the current in the oscillatory circuit, and therefore also the inductances of the induction-coil circuits. Probably this effect is more marked in the secondary than in the primary, since the latter circuit contains also considerable air-core inductance. In this way a very gradual variation of the tuning of the circuits can be effected. Occasionally the two notes, separated by a finite interval, were heard together in the telephone when the filament current was adjusted to a certain value.

In another experiment, with a different pair of generating coils and with the condensers and induction coil connected to the point X (fig. 1), matters proceeded rather differently when C_1 was varied. At 0.85 mfd., with the induction coil in circuit, a clear note was heard in the telephone, and the change of pitch at shortcircuiting indicated that L was negative. At 1.56 mfd. the note was about a perfect fifth lower in pitch, and at this value L was positive. But no note at all was heard with the inductance coil in circuit if C_1 was between these two values. It appears therefore that, in addition to the break of continuity in the variation of frequency which occurs when C_1 is gradually increased, there may also be an interval in the sequence of values of the capacity at which oscillations are audibly produced by the system. These effects will be considered later from another point of view, in connexion with the frequencies of the whole oscillatory circuit regarded as a coupled system.

When the high-tension transformer was substituted for the induction coil the rise of pitch at unshortcircuiting could be made much greater. Thus with $L_A = 0.086$ henry and $C_1 = 3.5$ mfd. the rise of pitch was about a minor sixth (see fig. 3), indicating an apparent self-inductance of about

* In the circumstances of this experiment the core of the induction coil was in a state well below that of maximum inductance, so that a diminution of current was accompanied by a diminution of L_1 .

—0.052 henry. The value of the coefficient λ for the transformer in the circumstances of this experiment was about 0.52. It may be found from the period and decrement of the oscillation of the secondary circuit with the primary open. Such oscillations may be produced by means of a battery and interrupter (without condenser) in the primary circuit. An oscillation of this kind (as shown by the electrostatic oscillograph) is given in fig. 11 (Pl. IV.), but the form of the curve, and in particular the ratio of the periods of the two half-waves which appear in it, varied considerably with the current used in starting the oscillations, as might be expected owing to the very variable inductance of a coil provided with a closed iron core. If the above value be assumed for λ it follows from condition (9) that the coupling of the transformer circuits must be at least as great as 0.92.

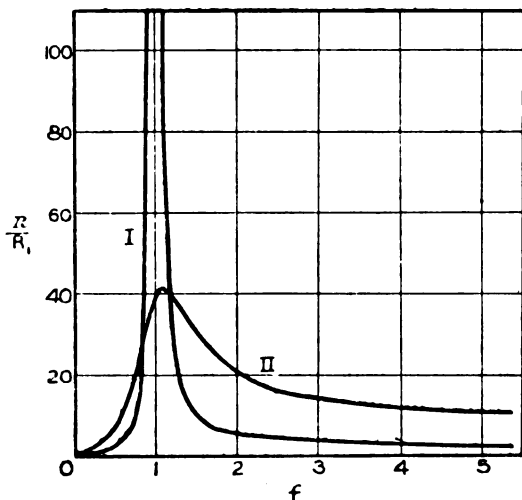
With the valves and coils used in these experiments it was not found possible to reduce the frequency sufficiently to produce with the transformer a discontinuity of pitch similar to that observed with the coil.

The experiments may be modified by connecting a variable condenser to the secondary terminals of the transformer. If C_2 is increased, both λ and f increase, and the effect is somewhat similar to that of diminishing C_1 . The primary capacity being kept constant, if C_2 is small the apparent inductance of the transformer is negative, if C_2 is large L is positive. At a certain value of the secondary capacity no change of pitch occurs when the transformer is short-circuited.

Turning now to the apparent resistance of the primary coil as given by (8), the variation of R/R_1 with f is shown in fig. 12 for the two numerical cases of fig. 10, the value of R_1/L_1 being taken as 149 in both cases. Curve I. is the curve for the smaller secondary resistance. In this case the ratio R/R_1 is unity at very low frequency, 2.109 at very high frequency, and has a sharp maximum of 216.3 (not shown in the diagram) at a frequency slightly greater than the resonance value. In curve II., calculated for the higher secondary resistance, the variation is much more gradual, the maximum being about 41.6 at $f=1.1$, but the region of high apparent resistance extends to frequencies differing more widely from the resonance value. The fact that the apparent resistance of the primary coil of a transformer may be very great at and near the resonance frequency is of fundamental importance in connexion with the question, to

be discussed later, of the maintenance of the oscillations of the whole coupled system.

Fig. 12.



3. Energy Relations.

It is of interest to consider the energy relations of the transformer system in connexion with the apparent inductance and resistance of the primary. Since L is sometimes negative it is clear that the expression $\frac{1}{2}Li_1^2$ cannot represent the electrokinetic energy of the transformer circuits, or the total energy of the circuits, both of which quantities are always positive. To simplify the matter we will suppose that $L_{12}=L_{21}=M$, and in the first place neglect the resistances.

Equation (4) may now be written

$$L \frac{di_1}{dt} = E \cos pt, \quad . \quad . \quad . \quad (13)$$

and by (2) and (3)

$$i_2 = \frac{MC_2 p^2}{1-f} i_1. \quad . \quad . \quad . \quad (14)$$

The electrokinetic energy of the primary coil is therefore

$$\begin{aligned} \frac{1}{2} i_1 (L_1 i_1 + M i_2) &= \frac{1}{2} i_1^2 \left(L_1 + \frac{M_2 C_2 p^2}{1-f} \right) \\ &= \frac{1}{2} L_1 i_1^2 \left(1 + \frac{k^2 f}{1-f} \right) \\ &= \frac{1}{2} L_1 i_1^2 \quad . \quad . \quad . \quad (15) \end{aligned}$$

by (12).

The electrostatic energy in the secondary circuit expressed in terms of the primary current is

$$\frac{1}{2} C_2 V_2^2 = \frac{1}{2} \frac{k^2 L_1 f}{(1-f)^2} (i_0^2 - i_1^2), \quad . \quad . \quad . \quad (16)$$

where i_0 is the maximum value of the primary current.

Substituting from (14) and (16) in the expression for the total energy of the transformer circuits, we find after reduction

$$\begin{aligned} \frac{1}{2} L_1 i_1^2 + M i_1 i_2 + \frac{1}{2} L_2 i_2^2 + \frac{1}{2} C_2 V_2^2 \\ = \frac{1}{2} L i_1^2 + \frac{1}{2} \frac{k^2 L_1 f}{(1-f)^2} i_0^2, \quad . \quad . \quad (17) \end{aligned}$$

The second term on the right-hand side of (17) represents the electrostatic energy in the secondary circuit at the moment when the primary current is zero, and it is then the total energy of the transformer system.

From (15) and (17) we see that the expression $\frac{1}{2} L i_1^2$ may be regarded as representing (1) the electrokinetic energy of the primary coil of the transformer, (2) the increase of the total energy of the transformer circuits during the growth of the primary current from 0 to i_1 . Both of these statements are consistent with the result that by (13) the work done on the system by the applied E.M.F. during the growth of the primary current from 0 to i_1 is $\frac{1}{2} L i_1^2$.

Now bringing in the resistances we will calculate the total energy dissipated in the transformer circuits during one period T of the forced oscillation. If t be measured from a moment at which the primary current is zero, the expression for this current may be written

$$i_1 = A \sin \rho t.$$

The energy dissipated in the primary circuit is

$$\int_0^T R_1 i_1^2 dt = R_1 i_s^2 T,$$

i_s being the R.M.S. primary current.

The secondary current is given by

$$i_2 = \frac{M \rho^2 C_2}{\{(1-f)^2 + \lambda^2 f\}^{1/2}} A \sin (\rho t - \gamma),$$

where $\tan \gamma = \frac{R_2 C_2 \rho}{1-f}.$

The energy dissipated in the secondary circuit during one period is therefore

$$\begin{aligned}\int_0^T R_2 i_2^2 dt &= \frac{T}{2} \frac{R_2 k^2 I_1 I_2 C_2^2 \rho^4 A^2}{(1-f)^2 + \lambda f} \\ &= \frac{R_2}{L_2} \cdot \frac{k^2 I_1 f^2}{(1-f)^2 + \lambda f} i_s^2 T.\end{aligned}$$

Consequently the total energy dissipated in one period is

$$\begin{aligned}\int_0^T (R_1 i_1^2 + R_2 i_2^2) dt &= R_1 \left\{ 1 + \frac{k^2 I_1}{R_1} \cdot \frac{R_2 f^2}{(1-f)^2 + \lambda f} \right\} i_s^2 T \\ &= R i_s^2 T. \dots \text{by (8).}\end{aligned}$$

The expression $R i_s^2$ therefore represents the mean rate of dissipation of energy in both circuits of the transformer during the forced oscillations. It also represents the mean rate at which work must be done on the system by the applied E.M.F. in order to maintain the oscillations. If R is very great, as it may be when the frequency is near the resonance value, it is clear that a valve, to which energy is supplied at a limited rate, may for this reason fail to maintain oscillations of appreciable amplitude in the transformer.

4. The Oscillatory Circuit as a Coupled System.

In considering the action of the transformer we have regarded this portion of the oscillatory circuit as executing forced oscillations under the action of an applied E.M.F. of frequency n ($= \rho/2\pi$). When we deal with the whole oscillatory circuit, however, we must regard n as a natural frequency, since it is determined almost entirely by the constants of the circuit.

The system possesses two natural frequencies of oscillation given (if resistances are neglected) by the well-known equation

$$\begin{aligned}8\pi^2 n^2 &= \frac{1}{1-K^2} \left\{ \frac{1}{l_1 C_1} + \frac{1}{L_2 C_2} \right. \\ &\quad \left. \pm \sqrt{\left(\frac{1}{l_1 C_1} - \frac{1}{L_2 C_2} \right)^2 + 4K^2 \frac{1}{l_1 C_1} \frac{1}{L_2 C_2}} \right\}, \quad (18)\end{aligned}$$

where l_1 is the self-inductance of the primary circuit, $L_1 + L_2$, and K^2 is the coupling of the two circuits forming the whole system, *i. e.*

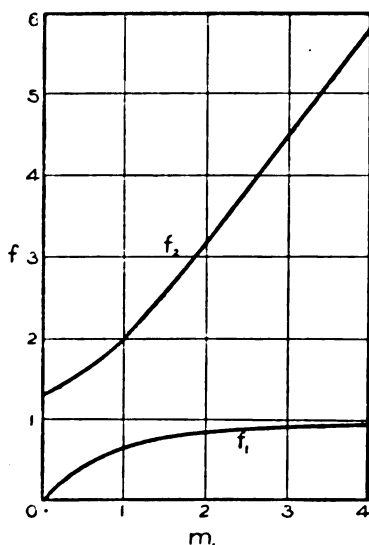
$$K^2 = L_{21} L_{12} / l_1 L_2.$$

If L_2C_2/l_1C_1 be denoted by m , the ratios of the squares of the frequencies of these oscillations to the square of the frequency of the secondary circuit when oscillating alone are given by

$$\begin{aligned} f_1 &= 4\pi^2 n_1^2 L_2 C_2 = \frac{1}{2(1-K^2)} \left\{ m+1 - \sqrt{(m-1)^2 + 4K^2 m} \right\} \\ f_2 &= 4\pi^2 n_2^2 L_2 C_2 = \frac{1}{2(1-K^2)} \left\{ m+1 + \sqrt{(m-1)^2 + 4K^2 m} \right\} \end{aligned} \quad \dots (19)$$

The manner in which f_1 and f_2 vary with m is illustrated by the two curves in fig. 13, which represent values calculated

Fig. 13.



from (19) for the particular case $K^2=0.26$, the coupling found for one of the arrangements used in the present experiments. The curves show that f_1 and f_2 continually increase as m increases from zero. At first f_1 increases rapidly, afterwards more slowly, gradually approaching unity, but only attaining this value when m becomes infinite. On the other hand, f_2 begins at the value 1.3514 (*i.e.* $\frac{1}{1-K^2}$) and increases to infinity as m indefinitely increases.

It appears therefore that the system (supposed to have

resistances too small to affect the frequencies appreciably) never oscillates with a frequency lying between the values $1/2\pi\sqrt{L_2C_2}$ (the resonance frequency of the transformer) and $1/2\pi\sqrt{L_2C_2(1-K^2)}$, but that the frequency may have any value lying outside these limits*. Also the resonance frequency ($f=1$) only appears when m is very great, *e. g.* when $C_1=0$, that is, when the primary is on open circuit. It follows also that if the system oscillates with a frequency less than the resonance frequency of the transformer ($f<1$), this oscillation must be the slower of the two oscillations of the system; if the observed frequency is greater than the resonance value ($f>1$) this must be the more rapid component.

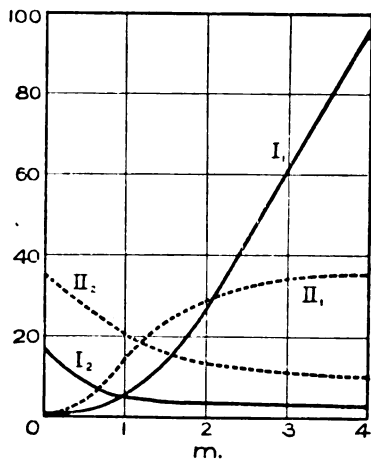
What happens in the valve experiment described on p. 633 is that when C_1 is increased from a small value (m diminishing) the note heard at first is the higher note of the system, but at a certain value of m not far from unity the note suddenly changes into the lower component and there is a sudden fall of pitch determined by the ratio of the two values of f for the value of m at which the change takes place.

It remains to be explained, however, why the two notes are not generally produced together, and why the lower note is heard when m is small (C_1 large), the higher note when m is large. For this purpose it is necessary to know the values of R , the apparent resistance of the transformer primary for various corresponding values of f_1 and f_2 . Taking again the two numerical cases of figs. 10 and 12, the values of R were calculated for the f_1 and f_2 corresponding to various values of m as shown in fig. 13. The results are shown in fig. 14, in which the full-line curves refer to the smaller secondary resistance ($\lambda=0.005147$). In fig. 14 curve I_1 shows values of R/R_1 for the oscillation of lower frequency (n_1) of the system, curve I_2 for the higher frequency (n_2). The curves extend over the range $m=0$ to $m=4$. It will be seen that when m is small the apparent resistance of the transformer primary is greater for the higher frequency than for the lower; when m is large R is greater for the lower frequency. The curves intersect at a value of m slightly greater than 1, and the values of R are varying rapidly at the point of

* It may be noticed that the range $f=1$ to $f=1/(1-K^2)$ is also that over which the apparent self inductance of the *whole oscillatory circuit* (excluding the condenser C_1) is negative. This follows from equation (12) on substitution of K^2 for k^2 .

intersection. Thus at $m=1.1$ the apparent resistance is nearly 40 per cent. greater for the lower frequency component than for the higher; at $m=0.9$ the apparent resistance is greater for the more rapid component in about the same ratio. At values of m more remote from unity the values of R for the two oscillations of the system differ much more. Thus at $m=1.5$, R is 3.5 times as great for the slower oscillation as for the more rapid; at $m=0.5$, R is over five times as great for the quicker component as for the slower. At the point of intersection the two equal values of R are each about $5.2 R_1$.

Fig. 14.



The broken line curves II_1 , II_2 in fig. 14 refer to the other numerical case ($\lambda=0.174$). These curves present similar features; when m is small the apparent resistance is much greater for the quicker component, when m is large it is much smaller for this component. The point of intersection of the curves II_1 , II_2 , occurs at a value of m slightly greater than 1.2, the equal values of R being about $18.5 R_1$. It appears that the value of m at which the apparent resistance of the transformer primary is the same for the two oscillations of the system is rather greater than unity, its excess above this value increasing with the resistance of the secondary coil.

When we remember that the condition for maintenance of valve oscillations depends upon the resistance of the oscillatory circuit—the addition of a few ohms to this

circuit is in some cases sufficient to stop the oscillations altogether,—it is easy to understand from the curves of fig. 14 why only one oscillation is usually maintained at a time, not both together, and why the slower component is the favoured one if m is small, the other if m is large*.

If the two oscillations of the system are ever maintained simultaneously this can only occur when the two values of R are equal or nearly so, that is, at the point of intersection of the curves,† and then only if the value of R at the intersection is not too great. If R is too great at the intersection no oscillations may be produced in appreciable intensity unless m is either considerably smaller or considerably greater than unity.

Since the frequency ratio n_2/n_1 of a system having given coupling is smallest when $m=1$, we may conclude that the two oscillations of the system can only be maintained simultaneously when the ratio of their frequencies is nearly at its minimum.

In former papers‡ the writer has shown that similar effects are produced when a pair of coupled oscillatory circuits are associated with a singing arc. In this arrangement also one note only is, as a rule, produced, this being the lower note of the system if m has less than a certain value (not far from unity), and the higher note if m is greater than the critical value. In certain cases both notes may be produced simultaneously (*loc. cit.* p. 719), accompanied by their difference-tone, which is unusually prominent in these circumstances.

An examination of the curves of fig. 13 shows that if the telephone note undergoes no change of pitch when the transformer is switched into the circuit of fig. 1, this can

* It is well known that a valve fails to generate oscillations if the self-inductance in the primary circuit exceeds a certain value depending upon the other constants of the circuit. It might therefore be thought that the extinction of one of the component oscillations is due to the increase of L near the resonance point (see fig. 10). This supposition would, however, not account for the facts. For if L is large and positive, f must be less than 1, and the frequency must consequently be that of the slower component (see fig. 13). If the increased apparent self-inductance of the transformer primary were the cause of the extinction of one of the notes, this would always be the lower note.

† It is assumed that R_1 is not extremely small.

‡ *Phil. Mag.* Jan. 1909, p. 41; Nov. 1909, p. 713 (with M. Owen); Oct. 1910, p. 660 (with D. E. Roberts).

only happen if the frequency before admission of the transformer is identical with that of the quicker component of the vibration afterwards, since L is zero only at values of f greater than unity. It can also be easily verified, if resistances are neglected, that the condition $L=0$, i. e.

$$1 + \frac{k^2 f}{1-f} = 0,$$

is consistent with the condition that the frequency $1/2\pi\sqrt{L_A C_1}$ should be equal to the greater of the two frequencies (n_2) given by equation (18).

The explanation given above of the absence of one or other of the two component vibrations of the system applies only to the steady state some time after unshortcircuiting when the amplitude has become constant. In the period of transition following the introduction of the transformer, however, while the system is accommodating itself to its new conditions, there is evidence that the two components often exist together. This matter we will now proceed to consider.

5. *Transient Effects of throwing the Transformer into Circuit.*

We will suppose that the transformer is unshortcircuited at a moment when the condenser C_1 is at its maximum potential. At this instant there is no current or potential in the secondary circuit, and the conditions are very similar to those existing in the Tesla coil, which is excited by charging the condenser to a certain initial potential V_0 and allowing it to discharge through the primary coil.

Neglecting for the present the action of the valve in maintaining (or reducing the damping of) one or other of the two oscillations, we should expect that two damped oscillations are set going, the potential at the secondary terminals being given by the expression *

$$V_2 = \frac{L_2 C_1 V_0}{\{(l_1 C_1 - L_2 C_2)^2 + 4K^2 l_1 C_1 L_2 \}^{1/2}} \{e^{-k_1 t} \cos(2\pi n_1 t + e_1) - e^{-k_2 t} \cos(2\pi n_2 t + e_2)\}, \quad (20)$$

* Drude, *l. c.* p. 539.

where

$$\begin{aligned} k_1 &= 4\pi^2 n_1^2 \left(\frac{\theta_1 + \theta_2}{2} - \beta \right), \\ k_2 &= 4\pi^2 n_2^2 \left(-\frac{\theta_1 + \theta_2}{2} + \beta \right), \\ \theta_1 &= \frac{1}{2} r_1 C_1, \quad \theta_2 = \frac{1}{2} R_2 C_2, \\ \beta &= -\frac{2\pi^2 n_1^2 n_2^2}{n_2^2 - n_1^2} (\theta_1 - \theta_2) (l_1 C_1 - L_2 C_2), \\ \sin e_1 &= \frac{2\beta + \frac{n_2 - n_1}{n_2} \delta}{\frac{n_2 - n_1}{2\pi n_1 n_2} - 4\pi\beta n_1 \delta}, \\ \sin e_2 &= \frac{2\beta + \frac{n_2 - n_1}{n_1} \delta}{\frac{n_2 - n_1}{2\pi n_1 n_2} - 4\pi\beta n_2 \delta}, \\ \delta &= \frac{\theta_1 + \theta_2}{2} + \beta \frac{n_2 - n_1}{n_2 + n_1}, \end{aligned}$$

and r_1 is the resistance of the whole primary circuit.

According to (20) the two components of the wave of secondary potential have equal initial amplitudes and different damping factors. In the primary circuit also we should expect the wave-forms of potential and current to consist of two components having damping factors k_1 and k_2 and different initial amplitudes. It can be shown that the initial amplitudes of the components in the primary current variation are

$$\text{and } \left. \begin{aligned} &\frac{2\pi n_1^3 (4\pi^2 n_2^2 l_1 (C_1 - 1))}{n_2^2 - n_1^2} V_0 \\ &\frac{2\pi n_2^3 (1 - 4\pi^2 n_1^2 l_1 (C_1))}{n_2^2 - n_1^2} V_0 \end{aligned} \right\} \cdot \cdot \cdot \cdot (21)$$

Fig. 15 (Pl. IV.) is an example of the curves shown by the electrostatic oscillograph, connected to the secondary terminals as in fig. 1, when the key K was opened. In this experiment the induction coil was used in place of the transformer owing to its greater suitability for inductance measurements. The periodic variations of amplitude in the curve of fig. 15 show clearly that two oscillations differing in frequency are present in the wave of secondary potential following the admission of the induction coil into the circuit.

The wave form shows considerable variations however, depending upon the phase of the previously existing oscillation at which the induction coil is switched in. If contact is broken at K at a moment when current is flowing into the condenser, a spark appears at the interrupter and the amplitude of the curve is small. The amplitude is greatest when contact is broken at a moment of maximum potential in C_1 , and when consequently no spark appears at K. The curve shown in fig. 15 was the curve of greatest amplitude among twenty photographs obtained with a certain combination of coils and condensers, all taken with the same current (indicated by a hot-wire ammeter) flowing in the condenser circuit before admission of the induction coil.

The constants of the circuits were determined for about the mean currents flowing in the circuits during the decay of the oscillations *, and found to be as follows :—

$$\begin{aligned} l_1 C_1 &= 6.728 \cdot 10^{-8} \text{ c.g.s.}, & L_2 C_2 &= 1.014 \cdot 10^{-7} \text{ c.g.s.} \\ L_{21} &= 4.0 \text{ henries}, & K^2 &= 0.26. \\ r_1/l_1 &= 384, & R_2/L_2 &= 1310. \end{aligned}$$

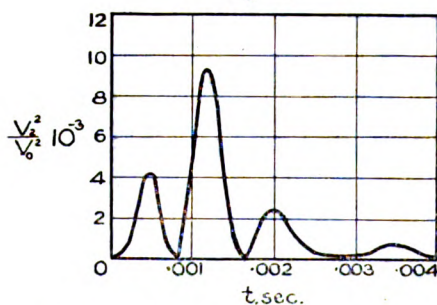
Calculated from these numerical values, the frequencies of the system are, by (18),

$$n_1 = 441.7, \quad n_2 = 806.7,$$

and the expression (20) for the secondary potential becomes

$$\begin{aligned} V_2 &= 95.5 V_0 e^{-383t} \cos(159000t + 1.2^\circ) \\ &\quad - 95.5 V_0 e^{-761t} \cos(290400t - 3.55^\circ). \end{aligned} \quad (22)$$

Fig. 16.



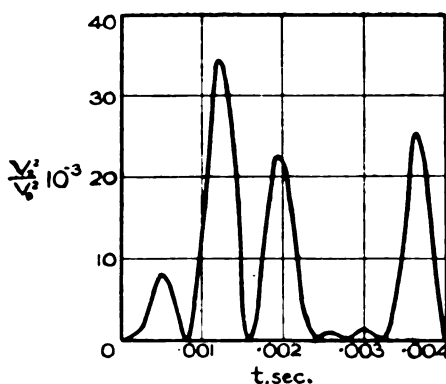
In fig. 16 is shown the curve representing values of V_2^2/V_0^2 calculated from (22) for various values of t , the time in seconds after admission of the induction coil. The

* Methods for determining the constants are given in 'The Theory of the Induction Coil,' Chap. VII. (1921).

curve indicates a maximum potential of $96.4V_0$ at the second peak, but the relative heights of the successive peaks in this curve do not agree well with those of the photograph in fig. 15.

For comparison, the curve was also calculated without allowance for damping ($k_1=k_2=0$). This undamped curve is shown in fig. 17. It indicates a much higher maximum potential, viz. $185.7V_0$, and a very different relation among the successive peaks.

Fig. 17



It is clear that fig. 17 indicates too high a maximum potential since it neglects damping altogether, while the maximum in fig. 16 is too small since it takes no account of the action of the valve in tending to maintain the more rapid oscillation. In the circumstances of the experiment the valve was unable to maintain this oscillation at a constant amplitude, but it considerably reduced its decrement.

The best plan that suggested itself at this stage was to determine the decrement k_2 of the rapid component directly from the curve of primary current (similar to fig. 3), since this curve apparently showed a single damped oscillation of frequency n_2 . When this curve was carefully examined it indicated a frequency 807.4 , which agrees satisfactorily with the calculated value of n_2 stated above (806.7); but its decrement showed considerable irregularity which may have been due to a slower superposed oscillation of small amplitude.

By (21) the ratio of the initial amplitudes of the slow and

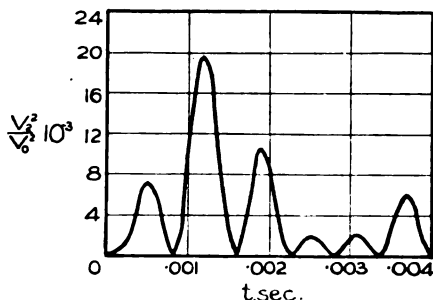
646 Prof. E. Taylor Jones on *Valve-generated*
rapid components in the primary current wave is

$$\frac{n_1^3}{n_2^3} \cdot \frac{4\pi^2 n_2^2 l_1 C_1 - 1}{1 - 4\pi^2 n_1^2 l_1 C_1}.$$

In the present case this fraction is equal to 0.248, so that the initial amplitude of the slower component in the primary current is only about a quarter of that of the rapid component, while its decrement is considerably the greater of the two. The observed irregularities in the decrement of the current curve were, however, not quite so great as might be expected to arise from a superposed oscillation of frequency 441.7, damping factor 383, and initial amplitude one quarter of that of the rapid component.

The mean decrement determined from the first two periods of the current curve, covering the time occupied by the first group of waves in fig. 17, was 105. With this value of k_2 employed in the calculation (instead of 761) and all other coefficients as in (22), the calculated curve becomes that shown in fig. 18. The agreement with the photographed

Fig. 18.



curve of fig. 15 is now much closer, though the damping of the rapid component in fig. 18 is still rather overestimated.

The maximum potential indicated in fig. 18 is $140.3V_0$, V_0 being the maximum potential of the primary condenser in the oscillations preceding the admission of the induction coil.

Now the smallest R.M.S. current which was observed to give at unshortcircuiting a 1 cm. spark between two metal spheres of 2 cm. diameter connected with the secondary terminals was 1.57 amperes. Also the frequency

FIG. 2.

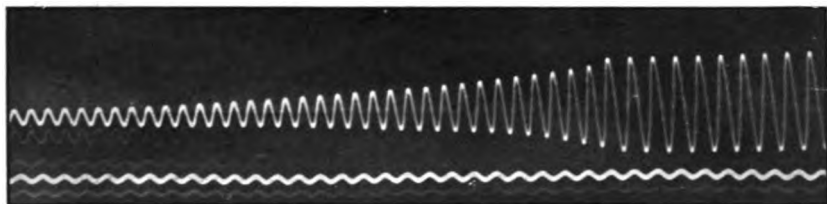


FIG. 3.

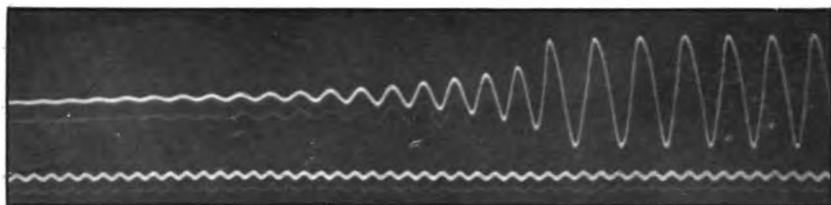


FIG. 4.

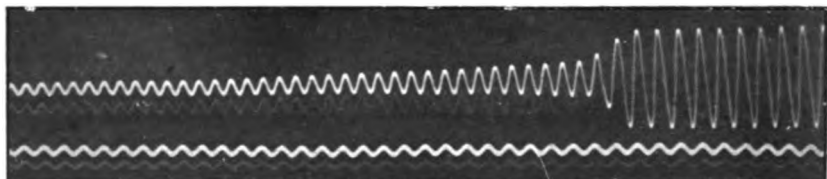


FIG. 5.

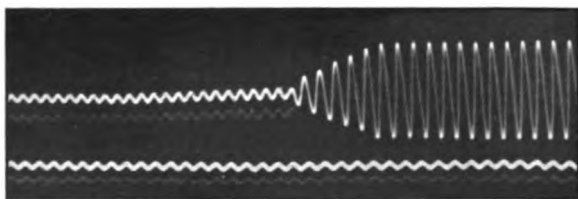


FIG. 6.

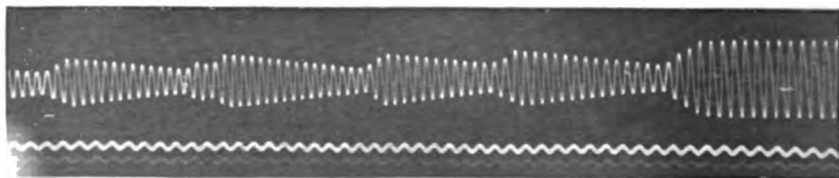


FIG. 7.



FIG. 8.

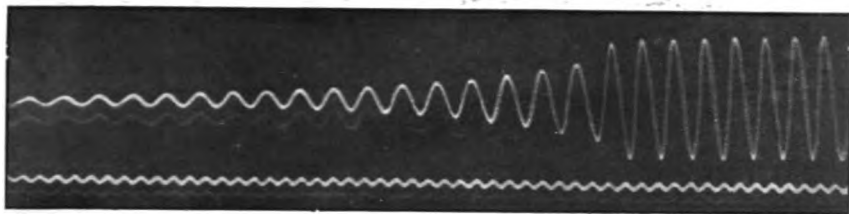


FIG. 9.

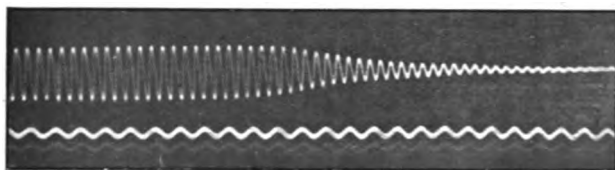


FIG. 11.

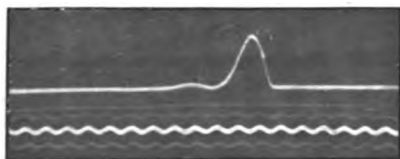
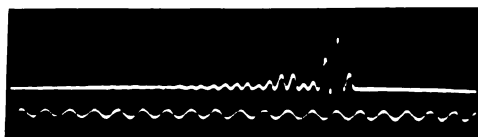


FIG. 15.



of the preceding oscillations was 753·6, and the capacity of the primary condenser 2·17 mfd. Consequently the value of V_0 in this experiment was

$$V_0 = \frac{1.57 \sqrt{2} \cdot 10^6}{2\pi \cdot 753.6 \cdot 2.17}$$

$$= 216 \text{ volts.}$$

The calculated maximum secondary potential is therefore

$$V_{2m} = 140.3 \times 216$$

$$= 30300 \text{ volts,}$$

which does not fall far short of the generally accepted value of 31000 volts required to spark across a 1 cm. gap of this kind.

It may be concluded that the method here adopted of substituting the observed damping coefficient k_2 of the quicker component, for the calculated value, in the expression for V_2 derived from the theory of the Tesla coil leads to a value for the maximum secondary potential at unshortcircuiting which agrees satisfactorily with experiment.

The effect of the valve in this experiment therefore appears to be, while leaving the damping of the slower component oscillation unaltered, to reduce considerably that of the more rapid component. In this way the valve raises the maximum secondary potential from $96.4V_0$, the value which it would have if both oscillations were subject to their own natural damping, to $140.3V_0$. The valve therefore serves the double purpose of first raising the primary condenser to a certain potential, and then increasing the ratio in which this potential is transformed in the secondary circuit.

The highest potential which it has been found possible to produce by the method of unshortcircuiting with the apparatus used in these experiments was 43000 volts. Probably much higher potentials can be attained by this method with more powerful valves.

Bangor, January 1924.

LIX. *The Fluorescence of Æsculin Solutions.*

By Miss M. B. KEARNEY, M.A.*

[Plate V.]

1. *Introduction.*

A CONSIDERABLE amount of work has been done recently on the fluorescence of organic solutions and the destruction of their fluorescent power by light. Perrin† has presented the view that the emission of fluorescence by organic substances is due to the flashes of exploded molecules; thus a molecule, having once emitted fluorescent light, has completely lost its power of fluorescence.

Wood‡, working on the transformation of fluorescent solutions by concentrated sunlight, was unable to obtain satisfactory confirmation of Perrin's theory. He found that a solution of rhodamine could be transformed without the emission of fluorescence by maintaining it at a temperature of 100° C.

Pringsheim§ carried out some experiments with fluorescein and eosin in various solvents and obtained results not capable of explanation by Perrin's hypothesis. He found that lowering of the temperature to -180° C., while retarding the photochemical action, had no influence on the intensity of the fluorescence. From theoretical considerations he regards Perrin's theory as unsatisfactory, since it places the fluorescence of organic solutions in a class separate from all analogous phenomena. He does not give any definite hypothesis as to the cause of fluorescence, but suggests that the molecules are excited by the absorption of light; from the excited state they either revert, with the emission of fluorescence, into the normal state or react chemically with other excited molecules and do not produce luminescence.

Kautsky and Zocher|| have made observations on the luminescence of unsaturated silicon compounds which are in agreement with Pringsheim's results, especially in regard to the dependence of the phenomenon on temperature.

* Communicated by Professor J. C. McLennan, F.R.S.

† J. Perrin, *Ann. de Phys.* (ix.), 10, pp. 133-159, Sept.-Oct. 1918.

‡ R. W. Wood, *Phil. Mag.* pp. 757-765, April 1922.

§ P. Pringsheim, *Zeits. f. Phys.* x. pp. 176-184 (1922).

|| Kautsky and Zocher, *Zeits. f. Phys.* ix. pp. 267-284 (1922).

In a paper recently published by McLennan and Cale* are given the results of an investigation of the fluorescence of dilute aqueous solutions of æsculin. The interesting point is brought out that an aqueous solution of æsculin can be made to fluoresce for a long time without destruction of its fluorescence when excited by light of suitable wave-length.

In view of this work some further experiments have been made on the fluorescence of æsculin solutions, with the hope of extending our knowledge of the subject.

2. Apparatus and Method.

The method of transforming and testing solutions of æsculin was similar to that used by McLennan and Cale. Transformations were effected by exposure of the solutions to a quartz mercury arc lamp 35 cm. long and carrying about 5 amps. Two solutions were generally transformed simultaneously; these were placed symmetrically with respect to the lamp at a distance of 4 cm. from its axis.

A Nutting spectrophotometer was used to measure the intensity of the fluorescent light. The arrangement of the apparatus was as follows:—Light from a self-regulating carbon arc lamp, after passing through condensing lenses and a nickel oxide glass filter, was reflected downward by a mirror into two test-tubes, placed horizontally, which contained the fluorescent solutions. The fluorescent light passed through a slit and entered the openings of the photometer.

The width of the slit used throughout the course of the experiments was 5 mm. On account of the reflexion of light from the curved surfaces of the tubes containing the solutions, the fluorescent intensity of 5 mm. thickness of solution in the central portion of the tube was measured. The solutions were sufficiently dilute to show no noticeable absorption at this depth.

The standard solution was taken as 4 parts of æsculin to 100,000 parts of solvent by weight, and the intensity of the fluorescence emitted by a solution of strength 8/100,000,000 could be measured.

3. Experiments with Ultraviolet Light.

To verify the above-mentioned result of McLennan and Cale, aqueous solutions of æsculin, of strength 4/100,000, were sealed in two evacuated test-tubes, one of quartz and

* McLennan and Cale, Proc. Roy. Soc. London, A. cii. pp. 256-268 (1922).

one of glass. These were exposed to the light of a glass mercury arc-lamp for 20 hours, and measurements of the fluorescent intensity were taken every half-hour. A solution of the same concentration in a similar evacuated and sealed glass test-tube was used for comparison; this was compared with a freshly prepared solution four times during the experiment, and was found to have the same intensity every time. At the end of 20 hours neither solution which had been exposed showed any decrease in its fluorescent intensity.

This shows that none of the wave-lengths which are active in destroying the fluorescent power are transmitted by glass, whereas some, at least, of those causing fluorescence are in this region.

In a second experiment, solutions of *æsculin* in various solvents were exposed in evacuated and sealed quartz tubes to the light from a quartz mercury arc-lamp, and measurements were made of the fluorescent intensity at regular intervals during the exposure. The solvents used were water, ethyl alcohol, methyl alcohol, acetone, and glycerine; the initial concentration in every case was the same as that of the standard solution.

In sealing the quartz tubes after they were evacuated, precautions were taken to try to prevent ultraviolet light from the oxygen flame from penetrating the tubes and transforming the solutions. There was, however, sufficient light from the flame to cause a partial and easily measurable transformation, since, during the first few seconds of exposure, the rate of transformation is greatest. In order to obtain the initial portions of the decay curves solutions were exposed in corked quartz tubes.

Typical curves, showing the relation between intensity of fluorescence and length of exposure are shown in figs. 1 and 2.

Some characteristics of the curves noted are:—

(a) The initial fluorescent intensity was less for solutions in organic solvents than for aqueous solutions of the same concentration.

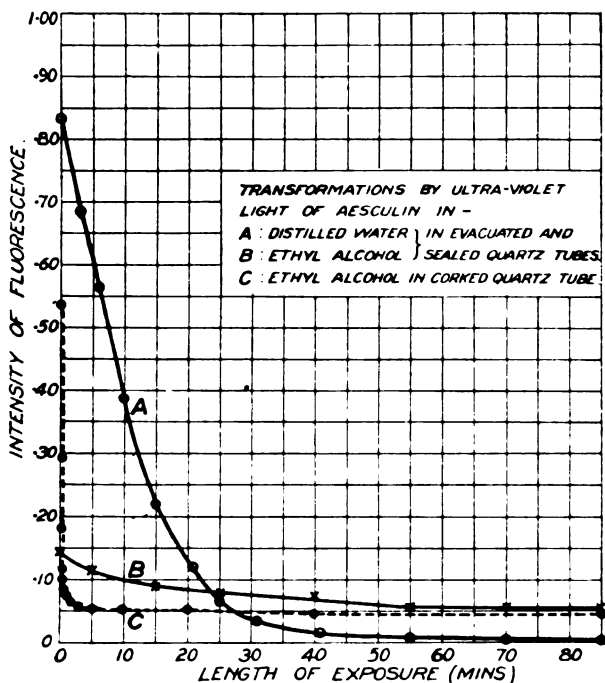
(b) For the first-mentioned solvents the initial portions of the decay curves showed a greater rate of transformation than that shown by the aqueous solution, whereas during the later part of the decay period the rate of transformation was less than that of an aqueous solution.

(c) Solutions in organic solvents required a much longer time of exposure to become completely transformed than those in water. A solution of *æsculin* in ethyl alcohol was

exposed for 18 hours before its fluorescence became too weak to be measured photometrically ; from fig. 1A it will be seen that the time of exposure for complete transformation of the same volume of aqueous solution was about 90 minutes.

(d) With the glycerine solution there appears to be a diffusion effect not noticed with any of the other solutions.

Fig. 1.



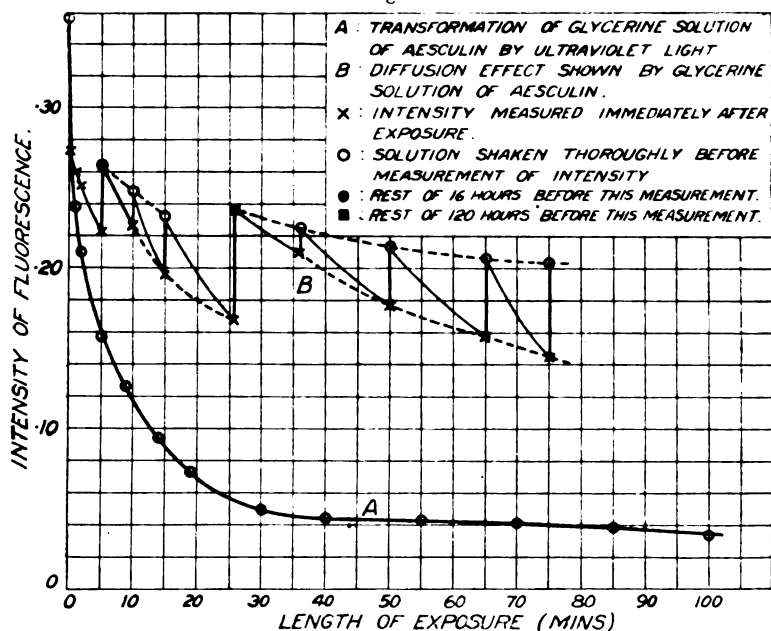
This is illustrated in fig. 2 B. After exposure for any period the intensity of fluorescence was found to depend on whether the solution had been shaken or not before being tested ; the same effect was obtained if the solution had been allowed to remain undisturbed for some time after exposure, and was probably due to the high coefficient of viscosity of glycerine.

4. Experiments with Ozone.

It has been noticed that aqueous solutions of *æsculin* are transformed by the passage of ozone through them, and that during the process of transformation an extremely faint bluish-white luminescence is emitted.

In order to obtain, if possible, a photograph of the spectrum of this glow, concentrated solutions of æsculin in water, acetone, glycerine, ethyl, methyl, and propyl alcohols were transformed by ozone. For every solution the intensity of the glow was extremely faint compared with the fluorescence of the solution under the action of ultraviolet light, so that

Fig. 2.



all observations had to be made in a darkened room. The following table gives roughly the relative intensities of the glows, distilled water being taken as the standard solvent:—

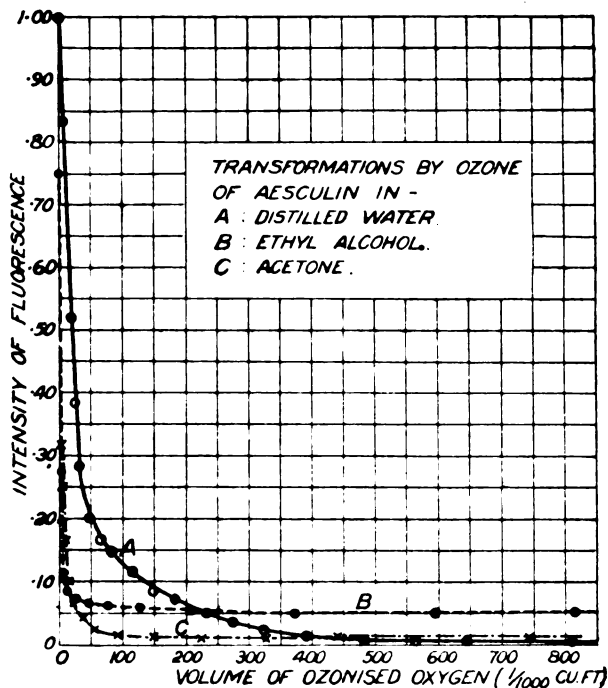
Solvent.	Intensity of Glow.
Ethyl Alcohol	5
Propyl Alcohol ...	5
Methyl Alcohol	3
Acetone	3
Distilled Water	1
Glycerine	0

The glow was brightest when ozone was first passed through a fresh solution, and decreased in intensity with further bubbling of ozone through it.

Ethyl alcohol was chosen as the most satisfactory solvent

with which to obtain the spectrum of the glow. A quartz tube was designed whereby a steady flow of fresh concentrated solution was maintained past an inlet for ozonized oxygen. A quartz spectrograph and a photographic plate most sensitive to blue light were used, but continued exposure for 9 hours produced nothing on the plate. As

Fig. 3.



the fluorescence spectrum was well brought out by a 20 minutes' exposure, the extreme faintness of the glow may be realized.

Photometric measurements were made of the fluorescent intensity of various solutions after the passage of known quantities of ozone through them. Fig. 3 shows the curves obtained for water, ethyl alcohol, and acetone. For the other solvents the curves are similar.

The intensity of the fluorescence of a glycerine solution was unaffected by the passage of ozone through it. Since no glow was produced in a glycerine solution, this would

seem to indicate that the glow is intimately associated with the decay of the fluorescent intensity. Another fact in support of this is that, during the initial rapid decay of the fluorescent intensity, the glow was brighter than it was when the rate of transformation had become small.

5. *Experiments with Æsculin Powder and at Low Temperature.*

It was thought that light might produce some effect on æsculin powder as well as on solutions. To test this, equal quantities (10 mgms.) of æsculin powder were spread evenly over the inner surfaces of evacuated quartz and glass tubes and were exposed to ultraviolet light for 50 hours. The tubes were then opened and the powder in each was dissolved in the same volume of distilled water. The fluorescent intensity of each solution was measured and showed no decrease with respect to the standard solution of the same concentration.

A similar experiment was performed with ozone. Through 10 mgms. of æsculin powder, 5 cubic feet of highly ozonized oxygen were passed. The solution prepared from this powder showed fluorescence equal to that of the standard solution.

This investigation was carried out with the view to experimenting at low temperatures, powder being more suitable than solutions for such work. The negative result prevented further work with powder, since the presence of a solvent is evidently necessary for the transformation of molecules of æsculin by ultraviolet light and ozone.

Since the freezing-point of pentane is below the temperature of liquid air, a solution of æsculin in pentane was prepared and its fluorescence was studied. At room temperature, it fluoresced weakly ; on lowering the temperature to that of liquid air, no change was observed in the intensity of the fluorescence. Pentane itself, however, showed fluorescence equal to that of the solution both at room and liquid-air temperatures.

6. *Absorption Spectra.*

Photographs of the absorption spectra of æsculin dissolved in glycerine and ethyl alcohol were obtained. Plate V. c and D show those obtained with glycerine solutions. The absorption spectra of fresh solutions of æsculin in glycerine

and ethyl alcohol had a band with maximum absorption at about $\lambda=3400\text{\AA}$. This band was narrower and less intensely absorbed for the organic than for aqueous solutions. Since it is supposed that the emission of fluorescence is associated with this band, the less intense absorption of these wave-lengths may account for the less intense fluorescence emitted initially by organic solutions as compared with that of an aqueous solution.

In the absorption spectra of transformed glycerine and ethyl alcohol solutions, however, there was a band with a maximum at about $\lambda=2700\text{\AA}$, which was not present in that of an aqueous solution.

Absorption spectra of solutions transformed by ultraviolet light were the same whether the transformation was effected in evacuated tubes or in contact with air. Solutions transformed with ozone have the same absorption spectra as those transformed by ultraviolet radiation.

7. Protective Action of Transformed on Fresh Solutions.

The absorption bands have been considered as indicating regions intimately related to the emission of fluorescence and the decay of the fluorescent intensity. In the absorption spectrum of an aqueous solution, it is supposed that the wave-lengths in both the bands are active in exciting fluorescence, and that those in the extreme ultraviolet band cause the decay of the fluorescent power as well.

If this be a correct interpretation, it would be expected that a fresh solution could be shielded from the radiation causing decay by surrounding it with a completely transformed solution which would absorb the wave-lengths in the ultraviolet band. To test this, a quartz tube containing a fresh aqueous solution of æsculin was suspended in a quartz flask filled with decayed solution. This system was exposed to ultraviolet light for six hours, tests of the fluorescent intensity being made every hour. Care was taken to prevent any portion of the tube, except that containing the solution, from being exposed. It was found that the fluorescence was just as intense after exposure as it was initially. During the exposure, the solution fluoresced brilliantly, due to the transmission of wave-lengths in the upper band.

To make certain that this result was not due merely to the decreased intensity of the light after passing through a considerable thickness of solution, distilled water was

substituted for the decayed solution and the experiment was repeated. At the end of an hour, the fluorescent intensity had decreased noticeably and, after five hours' exposure, it had fallen to about one-fourth its original value.

Some further work should be done on the protective action of glycerine and alcoholic solutions to ascertain whether the presence of the band at $\lambda=2700\text{\AA}$ causes any change in the shielding effect.

8. Summary.

1. The initial fluorescent intensity of a solution depends on the solvent used ; it is greater for aqueous solutions than for organic solutions of the same concentration.

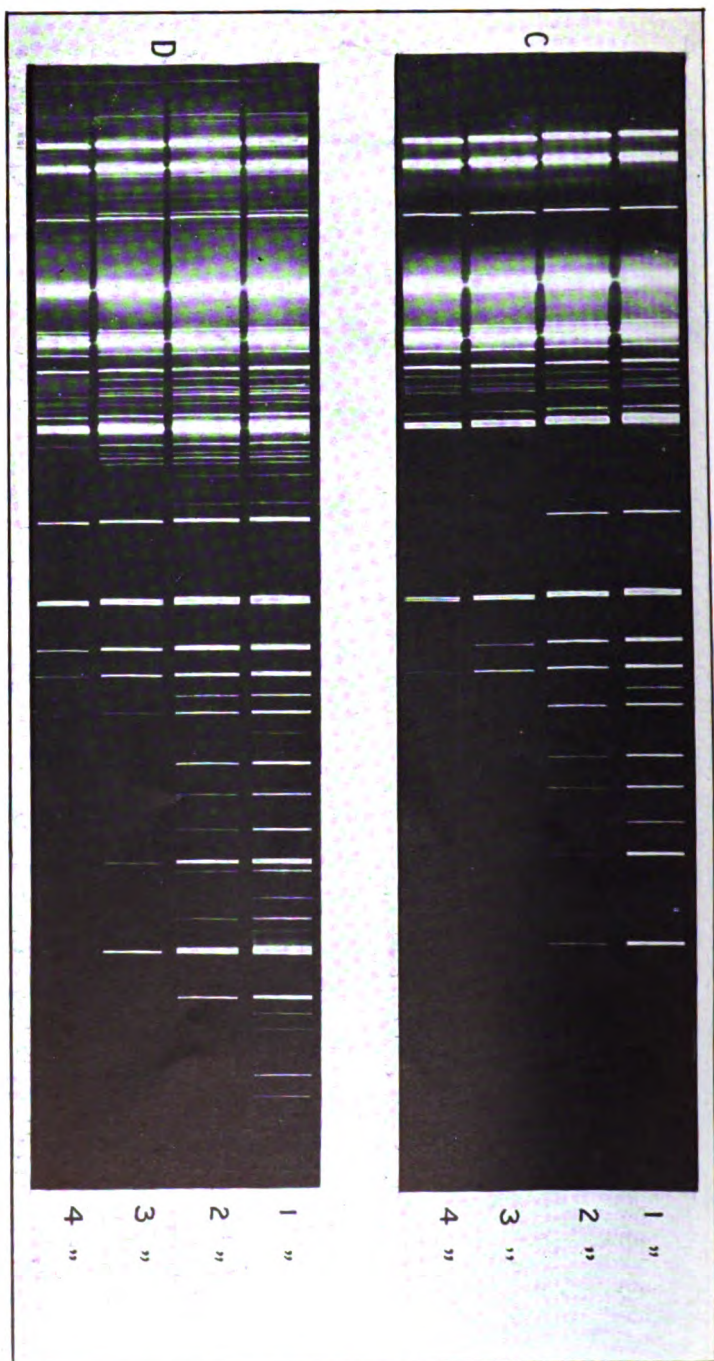
2. For solutions of equal concentration, the initial rate of transformation by ultraviolet light and ozone is greater for organic than for aqueous solutions, but organic solutions require a much longer exposure for complete transformation.

3. The presence of a solvent is essential for the transformation of æsculin ; ultraviolet light and ozone produce no change in æsculin powder.

4. It has been verified that a solution can be made to fluoresce without being destroyed by exposing it either in an evacuated glass tube, or in a quartz tube surrounded by a transformed solution. In both cases, the extreme ultraviolet wave-lengths are cut off, showing that the decay of the fluorescent intensity is due to the wave-lengths in the extreme ultraviolet region.

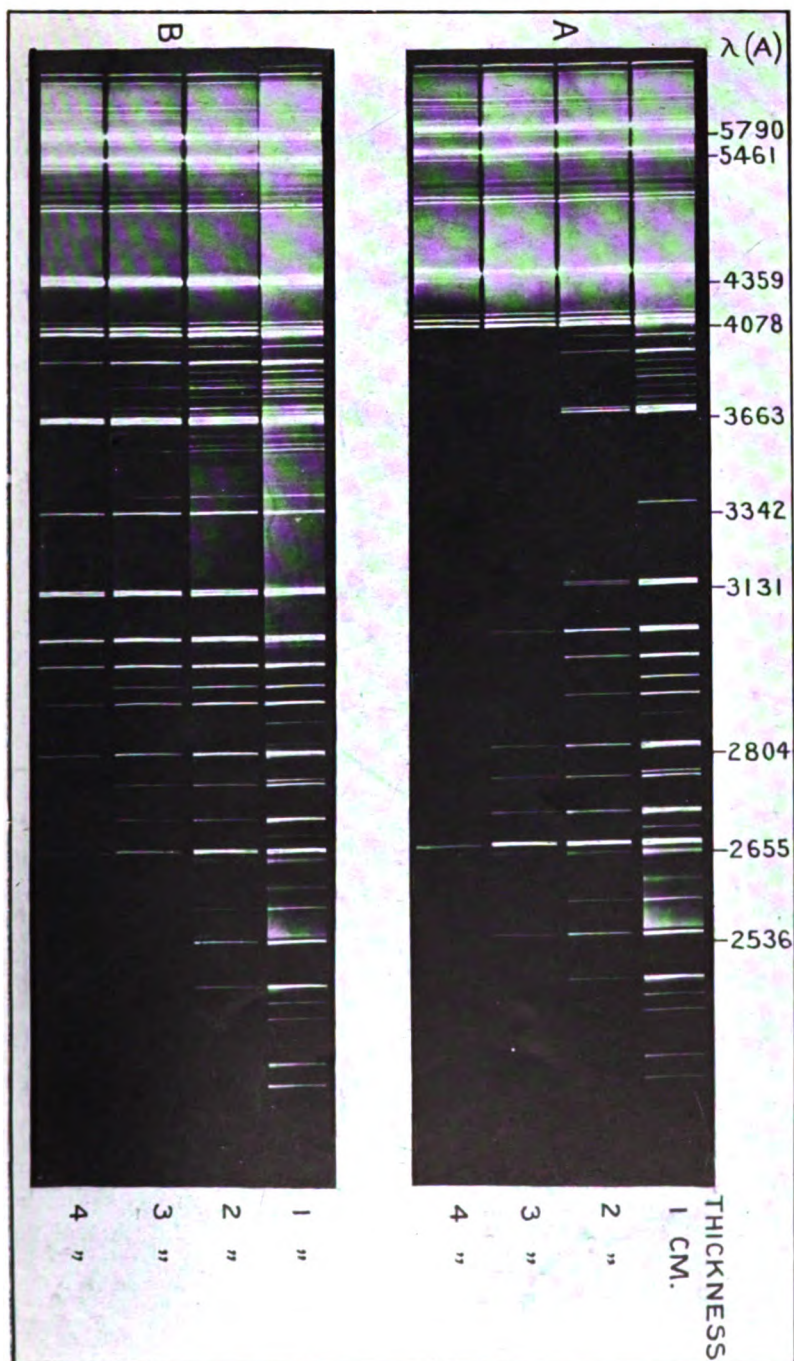
In conclusion, the writer wishes to express her sincere thanks to Professor J. C. McLennan for suggesting the problem and for his kindly interest, also to Mr. J. F. T. Young for his helpful suggestions. Thanks are due to the Honorary Advisory Council for Scientific and Industrial Research of Canada for the award of a Bursary by which the writer was enabled to carry out the investigation.

The Physical Laboratory,
University of Toronto.
May 30th, 1923.



ABSORPTION SPECTRA OF ESCULIN SOLUTIONS.

- A. Aqueous solution unexposed.
- B. " " decayed.
- C. Glycerine " unexposed.
- D. " " decayed.



LX. *The Crystal Structure of Metallic Arsenic.* By A. J. BRADLEY, M.Sc., *Research Student in Physics, The Physical Laboratories, The University, Manchester* *.

1. *Introductory.*

THE metallic form of arsenic is described by Groth†. It has a density of 5.727 (Bettendorf) or 5.71 (Petersen). It crystallizes in greyish crystals possessing the symmetry of the ditrigonal scalenohedral class (dihexagonal alternating) of the rhombohedral system. If the crystal be referred to hexagonal axes the axial ratio $a:c$ is 1:1.4025 (G. Rose). In this paper the three edges of the unit rhombohedron which meet in the trigonal axis will be taken as crystallographic axes. The angle θ (100):(010) = $94^{\circ} 56'$ (G. Rose). This corresponds to an angle $\gamma = 84^{\circ} 36'$ between the three axes, though by an arithmetical error Groth gives $85^{\circ} 38'$. The crystals when obtained by sublimation often twin parallel to the (110) face. Cleavage occurs most readily parallel to the (111) face, but it may also occur parallel to the (110) face.

Crystals of arsenic of this type are isomorphous with the corresponding crystals of antimony and bismuth. The structure of the former has been determined by R. W. James and N. Tunstall‡, and that of the latter by R. W. James§. The structures of both antimony and bismuth follow the same pattern, and from its resemblance to the other two elements arsenic was expected to have the same type of structure.

2. *Experimental Methods.*

The method adopted was that of the powder photograph. A Shearer X-ray tube with a copper anticathode was used, and the radiation so obtained was filtered through nickel foil. In this way a homogeneous beam of K_{α} copper radiation of wave-length 1.539×10^{-8} cm. was directed into the camera. This was cylindrical in shape with its axis vertical and its diameter was about one inch. The finely-powdered arsenic was made into a paste with fish-glue and

* Communicated by Prof. W. L. Bragg, F.R.S.

† *Chemische Kristallographie*, i. Teil 19.

‡ *Phil. Mag.* xl. p. 233 (1920).

§ *Phil. Mag.* xlii. p. 193 (1921).

mounted on a hair placed vertically at the centre of the camera. The thickness of the powder was about .1 mm. The beam of X-rays diverging from a gold slit about .1 mm. wide entirely surrounded the powder. The film was fastened round the circumference of the camera by rubber bands and was exposed to the radiation for about 45 minutes, the tube being run at 9 milliamperes and 30000 volts.

The film was measured by a travelling microscope and the figures so obtained are shown in Table I., Column I. s = distance measured on film between corresponding lines. These lines require to be corrected for a slight eccentricity in the position of the hair. The centre of the stick of powder was .2 mm. behind the axis of the camera, and therefore further away from the film than it should have been. This makes the measured values of s too great, the error being in each case $+(.40 \sin 2\theta)$ mm., where θ is the glancing angle of incidence. The corrected values for s are given in Column II. The diameter of the camera was 2.55 cm. This must be corrected for the thickness of the film. The film used in these experiments was sensitized on both sides and was .20 mm. thick. On wrapping the film round the camera, one side is stretched and the other contracts. The celluloid is sufficiently elastic to flatten out again after development. It has been assumed that the amount of contraction on the inner side is exactly equal to the expansion on the outer side. This is equivalent to assuming that the length of the centre of the film is invariable. The effective radius of the camera was taken as the distance from the centre of the powder to the centre of the film, and was .10 mm. more than the actual radius. The effective diameter D was therefore 2.57 cm.

θ the glancing angle of incidence is given by

$$\theta = \frac{s}{4\pi D} \times 360^\circ = 1.111 s^\circ.$$

In Column V.,

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta} = \frac{.7695}{\sin \theta} \text{ \AA},$$

where d is the spacing of the atomic planes and n is the order of reflexion. $\lambda = 1.539 \text{ \AA}$ is the wave-length of the radiation.

The factors used in these calculations were checked from a photograph of rock-salt which gave a mean value of $5.633 \text{ \AA}$ for the side of a unit cube. The standard value is $5.628 \text{ \AA}$. The difference is less than 1 in 1000.

3. *General Form of Arsenic Structure.*

The structure of antimony and bismuth can best be visualized as two interpenetrating face-centred rhombohedral lattices related to one another in almost the same way as the sodium and chlorine lattices in rock-salt. The lattices regarded in this way are almost cubic, but are however slightly elongated parallel to a trigonal axis, and one lattice is slightly displaced with respect to the other in a direction parallel to the trigonal axis. The spectra observed in the case of arsenic admit of a similar explanation.

If the atoms of arsenic were arranged at the corners of a rhombohedron so that they lay on a simple rhombohedral lattice, we should have the simplest possible arrangement compatible with the crystallographic data. The unit cell would contain one atom of arsenic. From the data of Groth it is possible to calculate the length of side of a unit rhomb of this type. Taking the density of arsenic as 5.72, the length of side $a = 2.805 \text{ \AA}$. From a and γ all possible

values of $\frac{d}{n}$ down to $.850 \text{ \AA}$ were calculated. Reflexions

were found corresponding to almost all these values, but in addition there were lines on the film corresponding to twice the normal spacings in the case of odd planes such as (111), (311). This is the type of spectra peculiar to a face-centred structure, the length of side of a unit rhomb being $2a$ and each rhomb containing four atoms. The value obtained for a shows there are eight atoms of arsenic to each unit cell. The structure must consist of two interpenetrating face-

centred rhombohedral lattices. All values of $\frac{d}{n}$ for such a

system were calculated and compared with the observed values in Column V. They were found to be on an average 0.2 per cent. higher than the experimental values. The calculated values are given in Column VI., after allowing for this difference. The density as determined from X-ray data is 5.75, $a = 2.799$.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
s mm.	s (corrected) mm.	θ .	$\sin \theta$.	$\frac{d}{n}$ (Obs.) $\times 10^{-8}$ cm.	$\frac{d}{n}$ (Calc.) $\times 10^{-8}$ cm.	hkl .	Order of Intensity Obs.	Order of Intensity Calc.	Error.
1	11.41	12.50	.2164	3.555	3.529	111	19	19	...
2	12.8	14.0	.242	3.18	3.118	111	25	24	1
3	14.65	16.05	.2765	2.780	2.777	200	1	1	...
4	20.07	22.01	.3749	2.054	2.054	220	3	3	...
5	21.92	24.03	.4070	1.891	1.886	220	2	2	...
6	23.20	25.56	.4316	1.781	1.790	311	4	9	5
7	23.55	25.83	.4358	1.764	1.764	222	12	15	3
8	25.13	27.57	.4628	1.662	1.662	311	...	26	...
9	26.83	29.46	.4919	1.562	1.559	222	8	7	1
10	30.06	33.68	.5545	1.387	1.388	400	5	4	1
11	31.15	34.22	.5624	1.368	1.368	331	7	8	1
12	33.44	36.78	.5989	1.286	{ 1.291 1.287 }	{ 331 420 }	23	23	...
13	35.42	38.05	.6286	1.223	{ 1.227 1.226 }	{ 422 331 }	6	5	1
14	36.18	39.80	.6401	1.201	1.201	420	21	21	...
15	36.85	40.55	.6501	1.182	1.177	333			

16		39.45	39.05	43.45	.6877	1.119	1.119	4.22	9	6	3
17		39.97	39.57	44.00	.6947	1.107	1.109	5.11	14	14	...
18		40.82	40.42	44.95	.7065	1.089	1.088	4.22	15	15	...
19		41.96	41.56	46.15	.7211	1.068	1.066	5.11	20	22	2
20		43.27	42.87	47.65	.7390	1.041	{ 1.039 1.038 }	{ 3.33 5.11 }	24	25	1
21		44.27	43.87	48.75	.7516	1.023	1.027	4.40	...	28	...
22		45.82	45.43	50.50	.7716	.908	1.005	4.42	10	10	...
23		48.74	48.36	53.75	.8065	.955	.907	5.31	16	13	3
24		49.65	49.27	54.75	.8166	.942	.955	5.31	18	18	...
25		50.78	50.41	56.00	.8290	.929	.943	4.40	11	11	...
26		51.30	50.94	56.60	.8348	.922	{ .9265 .9265 }	{ 6.00 4.42 }	22	20	2
27		52.34	51.99	57.85	.8466	.908	.9215	5.33	13	12	1
28		54.00	53.65	59.70	.8634	.891	{ .910 .902 }	{ 5.31 6.20 }	...	27	...
29		58.12	57.81	64.30	.9011	.854	{ .895 .892 }	{ 6.22 4.42 }	17	17	...
Total Error										25	25

The agreement between Columns V. and VI. proves the nature of the space lattices of which the arsenic structure is built up, but throws no light on their mutual relationship. That they can only be displaced from a position of coincidence by a movement along the trigonal axis follows from considerations of symmetry. The most symmetrical arrangement would make the displacement exactly one-half of the length of the diagonal of the rhombohedral cell containing eight atoms of arsenic. This arrangement constitutes the simple rhombohedral structure which has already been shown to be impossible, since the spacing of planes with odd indices is doubled. The amount of displacement from this simple arrangement can only be determined from a consideration of the relative intensities of reflexion from the various planes of the crystal.

The intensity of reflexion from one lattice of arsenic only can be calculated as follows. For this purpose we must assume the validity of some empirical expression which will give the total intensity of reflexion for any one set of planes. In the case of rock-salt, W. H. Bragg* found that the intensity of reflexion falls off approximately with the square of the sine of the glancing angle, this relation including the progressive decrease in intensity of reflexion from each atom due to the distribution of its electrons. The intensity is further reduced by the effects of thermal agitation, but these only come into play in the case of very closely spaced planes. If we assume that the same law holds for arsenic and that the effect of thermal agitation in reducing the reflexion at large angles is negligible, we obtain the following expression for the intensity of reflexion from any plane (hkl) reflecting radiation at an angle θ :

$$I = \frac{NA}{\sin^2 \theta},$$

where A is a constant, being a function of the scattering power of arsenic, and N is the number of faces corresponding to the form $\{hkl\}$.

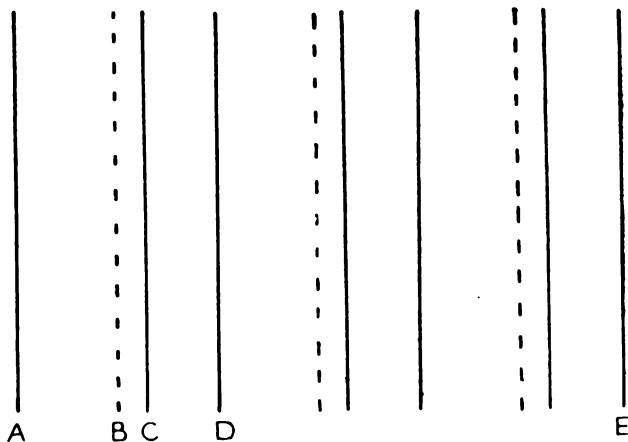
To obtain the combined effect of the two lattices allowance must be made for the phase difference between reflexions from atoms of different lattices. This phase difference is not the same for different planes, but it can easily be calculated for each case.

The arrangement of atoms in the 111 planes is represented in fig. 1. If the atoms were arranged on a simple rhombo-

* W. H. Bragg, *Phil. Mag.* xxvii. p. 881 (May 1914).

hedral lattice the spacing would be AB . The displacement of the plane of atoms from B to C doubles the spacing, which is now AD (d_{111}). There are three repetitions of AD as we pass along the diagonal of a unit cell from A to E , so that $AE=3AD$. Let the ratio of BC to AE be x . Then $BC=3x \cdot AD=3xd_{111}$.

Fig. 1.



The phase difference between A and D is $2n\pi$ for a n th order reflexion. The phase difference between A and C will be $2n\pi(\frac{1}{2} + 3x)$. As x increases, up to a certain limit the pairs of planes will approach closer together. If n is odd, the phase difference increases from an odd number of half-wave lengths to an even number, and the intensity of reflexion increases. If n is even the reverse is the case, and the intensity falls off.

The arrangement of atoms in the 100 planes is shown in fig. 2. Only half the atoms in each plane of the simple structure are displaced. The displacement of half the atoms in plane A to D does not affect the unit spacing of the planes. The spacing between opposite faces of the unit cell (d_{100}) is now AC , but there is no reflexion corresponding to this distance. The first reflexion will correspond to the spacing AB (d_{200}). As before, the distance $AD=xAC=xd_{100}$. The phase difference between A and C is $2n\pi$ for a n th order reflexion, but as B is exactly half way between A and C there will only be even order reflexions. The phase difference between A and D is $2n\pi x$. In this case, as x increases the

phase difference increases and the intensity lessens until it ultimately falls to zero.

All planes belong to either Class I. (Planes like (111)) or Class II. (Planes like (100)). The general formula for any

Fig. 2.



plane hkl can be obtained as follows. Taking the crystallographic axes as Cartesian axes, the positions of the atoms composing the structure may be represented thus :—

m, n, p	$m + x + \frac{1}{2}, n + x + \frac{1}{2}, p + x + \frac{1}{2}$
$m + \frac{1}{2}, n + \frac{1}{2}, p$	$m + x + 1, n + x + 1, p + x + \frac{1}{2}$
$m, n + \frac{1}{2}, p + \frac{1}{2}$	$m + x + \frac{1}{2}, n + x + 1, p + x + 1$
$m + \frac{1}{2}, n, p + \frac{1}{2}$	$m + x + 1, n + x + \frac{1}{2}, p + x + 1$

where m, n, p are integers and x is the displacement of the second lattice from the simple rhombohedron, as a fraction of the length of the long diagonal of the unit rhombohedron, which contains eight atoms of arsenic.

If $x_1y_1z_1$ be any point on the second lattice, its distance d from a plane hkl of the first lattice which passes through the origin is given by

$$d = (hx_1 + ky_1 + lz_1)d_{(hkl)},$$

where $d_{(hkl)}$ is the distance between planes (hkl) passing through the atoms m, n, p ; $m+1, n+1, p+1$, etc.

The distance between corresponding planes of the two lattices will therefore be

$$\begin{aligned} d &= (h(x + \frac{1}{2}) + k(x + \frac{1}{2}) + l(x + \frac{1}{2}))d_{hkl} \\ &= (x + \frac{1}{2})(h + k + l)d_{hkl}. \end{aligned}$$

If $x_2y_2z_2$ be any point on the first lattice, its distance d from any plane hkl of the same lattice passing through the origin is given by

$$d' = (hx_2 + ky_2 + lz_2)d_{hkl},$$

where d_{hkl} has the same meaning as before.

By giving $x_2y_2z_2$ different integral values we find that the distance between neighbouring planes d_1 is given by $d_1 = d_{hkl}$ for planes with odd indices (111, 311), $d_1 = \frac{1}{2}d_{hkl}$ for planes with mixed indices (100, 210). If there is a phase difference $2r\pi$ between waves reflected from neighbouring planes of the same lattice, r being an integer, reflexion will occur. Thus in the case of planes with mixed indices, d_{hkl} represents a phase difference $4r\pi$ and only even order reflexions will occur. With this proviso d_{hkl} always represents a phase difference $2n\pi$, where n is an integer representing the order of reflexion.

The spacing d will therefore represent a phase-lag $(x + \frac{1}{2})(h + k + l)2n\pi$. If we adopt the usual convention and incorporate the factor n in the indices hkl as has been done in Column VII., the phase-lag becomes $(x + \frac{1}{2})(h + k + l)2\pi$. This expression gives the phase difference between waves reflected from corresponding planes of different lattices. The amplitudes of the two waves are equal, so the total effect will be proportional to

$$[2 + 2 \cos (x + \frac{1}{2})(h + k + l)2\pi].$$

The total intensity of reflexion I will be given by

$$I = \frac{NA}{\sin^2\theta} [2 + 2 \cos (x + \frac{1}{2})(h + k + l)2\pi]. \quad . \quad . \quad (1)$$

The constant A can be omitted for comparative purposes. From this expression I was calculated for different planes and for various values of x from 0 to .075.

4. Evaluation of the Indeterminate Parameter x .

From equation (1) it follows that if $x=0$, the phase factor is zero if $(h+k+l)$ is odd and is equal to 4 if $(h+k+l)$ is even. These are minimum and maximum values respectively, and as x increases the values will change periodically.

For every value of x between 0 and .5 there is a different series of values for I , and in order to fix the most probable value of x it is only necessary to find the best agreement

between the observed intensities of reflexion and the calculated values of I . It is impossible to get absolute values of intensity by the photographic method, and comparative quantitative estimates of blackening are not easy to get photometrically, partly because of the difficulty of allowing for the background of general radiation, and also because of the varying widths of the lines and the feebleness of some of them. It is, however, much easier to arrange the lines in order of intensity of blackening. The intensity of blackening was estimated by viewing the film through a low-power microscope illuminated from below so that the lines showed up as much as possible. The line that appeared darkest in comparison with its background after allowing for its width was marked 1. The next darkest was marked 2 and so on. The results of this comparison are shown in Column VIII.

In order to test the validity of this method a comparison of the intensities of reflexion from rock-salt was made in this way. Assuming the law of the square of the cosecant to hold, we get in the case of rock-salt

$$I = \frac{N(F_{Na} + F_{Cl})^2}{\sin^2\theta} \quad \text{for planes with even indices,}$$

$$I = \frac{N(F_{Na} - F_{Cl})^2}{\sin^2\theta} \quad \text{for planes with odd indices,}$$

where I , N have the same meanings as before, and F_{Na} , F_{Cl} are proportional to the number of electrons in the ions of sodium and chlorine respectively. On comparing the intensities of reflexion so calculated with those obtained experimentally for the first twelve lines, it was found that they fell off in precisely the same order.

In the case of arsenic the intensities depend on the parameter x which may assume any value between certain limits. In order to guide us to an approximate value of x we must consider the peculiarities of one or two lines on the film. Lines 311, 442 and 444 entirely disappear. For the first line $h+k+l=1$, and the intensity of reflexion will be low for fairly small values of x , but not for medium or high values. Comparing this with 111 we again find a small reflexion showing x to be small. The lines 442, 444 disappear for

$$x = \frac{2n+1}{2} \frac{1}{h+k+l}$$

where n is an integer.

The smallest values giving zero reflexions are $x = \cdot 05$ and $x = \cdot 15$ for 442, and $x = \cdot 0417$ and $x = \cdot 125$ for 444. The line 200 is by far the brightest on the film. x must therefore be much less than $\cdot 25$, for which value the 200 reflexion disappears. The line 220 is the third strongest. It would disappear for $x = \cdot 125$ or $\cdot 375$. x must therefore be considerably less than $\cdot 125$. A value in the neighbourhood of $x = \cdot 04$ or $x = \cdot 05$ will fit in with all these facts.

Values of I were calculated for various values of x in the neighbourhood of $\cdot 05$, and for each value of x a table was arranged giving the intensities in descending order of magnitude. Column IX. shows the order for $x = \cdot 0488$. In the last column are given the difference between the calculated and observed orders in the case of each line. The arithmetic sum of these differences is 25. If x be given other values the divergency between observed and calculated values rapidly increases. This is shown in Table II., where the total difference between observed and calculated orders of intensity is given for various values of x .

TABLE II.

Displacement (x) ...	$\cdot 025$	$\cdot 04$	$\cdot 0425$	$\cdot 045$	$\cdot 046$	$\cdot 0475$	$\cdot 049$	$\cdot 0495$	$\cdot 05$	$\cdot 055$	$\cdot 06$	$\cdot 075$
Total error in Order of Intensity...	96	44	40	32	32	27	25	27	31	38	52	100

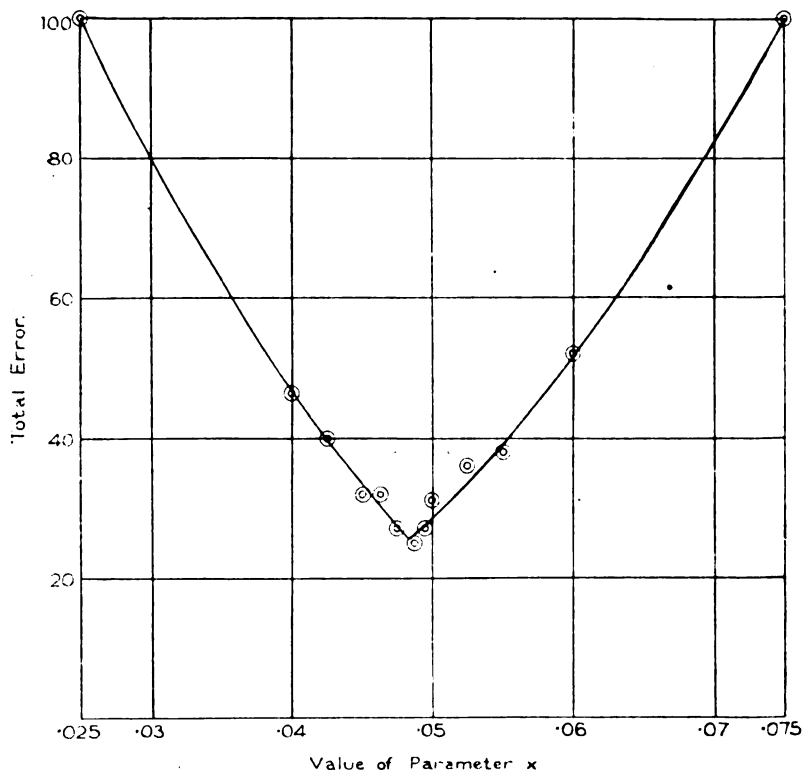
The data of Table II. are shown graphically in fig. 3. There is a very well marked minimum of error in the region $x = \cdot 0485$. This may therefore be taken as the most probable value of x .

James and Tunstall * expressed the value of the parameter as a fraction of the length of the diagonal of a rhombohedron containing only one atom of antimony or bi-muth. In order to compare the value here obtained for arsenic with those found for the other two metals it must therefore be doubled. We then have the value $x = \cdot 097$ as the ratio of displacement to length of diagonal of unit rhomb containing one atom of arsenic. The result is almost independent of the validity of the empirical law connecting the intensity with the sine of the glancing angle. This is true because those lines which increase or decrease in intensity with increase of x are scattered over the film quite promiscuously. The substitution of another empirical law will therefore scarcely alter that value of x which gives the best agreement between observed

* *Loc. cit.*

and calculated orders of intensity, but will merely decrease or increase the total error for every value of x alike. Actually, as the close agreement between Columns VIII. and IX. shows, the empirical law is very nearly true.

Fig. 3.



5. Comparison of Arsenic, Antimony, and Bismuth.

Each atom of arsenic has six nearest neighbours, three at a distance of 2.51×10^{-8} cm. and three at 3.15×10^{-8} cm. The three nearest lie in a plane (111) perpendicular to the trigonal axis and close to the parallel plane containing the first atom. The other three also lie in a plane perpendicular to the trigonal axis, but on the other side of the first atom and much farther away. In this way the whole structure is divided into double sets of planes separated by quite wide gaps from the next set. Cleavage naturally occurs

parallel to these planes (111). Table III. compares this and other properties in the case of the three elements.

TABLE III.

	As.	Sb.	Bi.
Edge of Unit Rhomb $2a$...	5.60 Å	6.20 Å	6.56 Å
Parameter $2x$...	.097	.074	.052
Longer Atomic Distance ...	3.15 Å	3.37 Å	3.47 Å
Shorter " " " ...	2.51 Å	2.87 Å	3.11 Å

The structure of arsenic, like that of antimony and bismuth, is a Sohncke point system. The two face-centred lattices of which it is composed are actually simple rhombohedral lattices of axial ratio 2.805 and length of edge of rhomb 4.145×10^{-8} cm. The structure is thus a special case of Sohncke's Point System No. 22—Das Zusammengesetzte Rhomboëdersystem. This simplifies to a system of point-pairs*, in which each point is at the centre of gravity of three of the original points. The two points of each pair are vertically above one another and are separated by a fraction $\frac{1}{2} + x$ of the distance between successive pairs.

In fig. 4 the plain circles represent atoms lying on a single lattice. If this be regarded as a face-centred lattice the rhombohedron ABCDEF is the unit. In this case $AB = 5.60 \text{ Å}$. There are four atoms of the first lattice to each unit rhomb and four of the second lattice (represented by shaded circles). The smaller and more acute rhombohedron AGHDJK is the unit cell of the structure regarding it as composed of two simple rhombohedral lattices. It contains only one atom of each lattice. $AG = 4.145 \text{ Å}$. The points LMNS of the second lattice correspond to the points AGKR of the first, and A and L constitute a point pair.

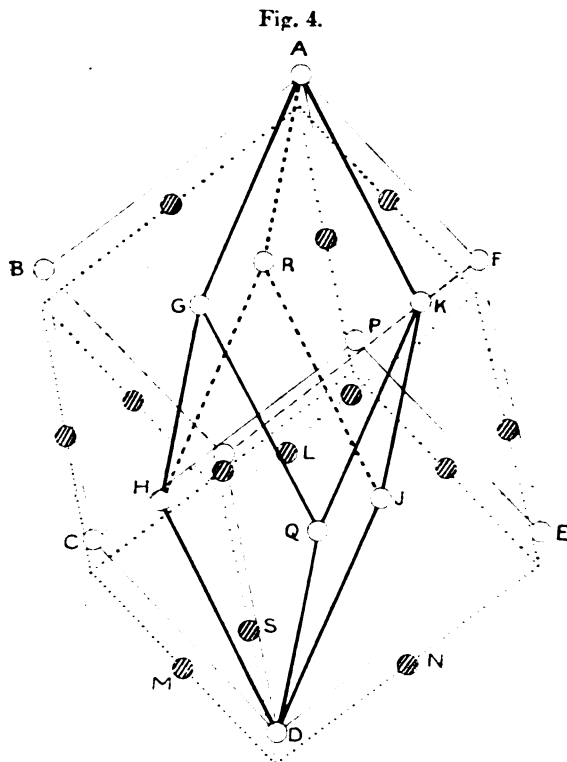
Summary.

The structure of metallic arsenic was found by the analysis of an X-ray spectrograph of the powdered material. The general form of the structure was the same as that of antimony and bismuth which had already been elucidated.

Measurements of the film agreed well with calculations made from the crystallographic data. The structure consists of two interpenetrating rhombohedral space lattices which

* Sohncke, *Entwicklung einer Theorie der Kristallstruktur*, 1871, p. 131.

together form a Sohncke point-system. In order to find the relationship between the two lattices it was necessary to evaluate the parameter x which fixes their relative position. For this purpose a comparison was made of the relative intensities of all lines on the film, and these were arranged



in descending order of intensity. The intensity of reflexion at any reflecting angle was calculated from a general formula for various values of x , and for each value the reflexions were arranged in order of intensity. On comparing these orders with that actually observed, one value of x was chosen as giving the best agreement. This parameter was found to be greater than for either antimony or bismuth. Finally, several properties of the three elements were tabulated. In all cases antimony was found to be intermediate in character between arsenic and bismuth.

The author wishes to express his gratitude for the kind advice and helpful suggestions given by Professor Bragg throughout the course of the work outlined in this paper. He also wishes to thank Dr. J. C. M. Brentano and Mr. H. E. Buckley, M.Sc., for their advice and assistance during the erection of the apparatus. Thanks are due to the Department of Scientific and Industrial Research for providing a grant which has enabled the author to carry out this work. The apparatus used in the research was purchased with the aid of grants made to the Physical Laboratory by the Government Grant Committee of the Royal Society, and by Messrs. Brunner Mond.

LXI. *On the Mean Distance between neighbouring Molecules in a Fluid.* By C. V. RAMAN*.

1. *Introduction.*

IN connexion with the theory of the scattering of X-rays in fluids developed by the author and Dr. Ramanathan in a recent paper †, it was found that the evaluation of the results required a knowledge of the mean distance between neighbouring molecules in a fluid. On reviewing the literature of molecular theory, it was found that the problem of finding this distance had been attempted, but not in an entirely adequate or satisfactory manner ‡. It is proposed, in this paper, to consider the question and it will be found that the discussion raises some points of interest in relation to the kinetic theory of fluids.

2. *Ideal Gases.*

The theory of dimensions suggests that the mean distance λ between neighbouring molecules could be expressed in terms of the number n of the molecules per unit volume of the fluid by a formula of the type $kn^{-1/3} = \lambda$, where k is a pure number. If we could postulate that the molecular centres occupy the corners of a cubical space-lattice, then obviously $k=1$. Actually, however, in a fluid, the arrangements of the molecules cannot be so definite, and k must,

* Communicated by the Author.

† Proceedings of the Indian Assn. for the Cultvn. of Science, vol. viii. part 2 (1923).

‡ P. Hertz, *Math. Annalen*, lxvii. p. 387 (1900); R. Gans, *Physikalische Zeitschrift*, xxiii. p. 100 (1922).

therefore, in general, differ from unity. For the case of an ideal gas, in which the distribution of the molecules is absolutely chaotic, λ may be evaluated in a perfectly rigorous manner. Consider any specified molecule A, and denote by $P(r)dr$ the probability that the nearest neighbour of A lies at a distance between r and $r+dr$ from it. Then the mean distance λ between A and its nearest neighbour is obtained by averaging, thus :—

$$\lambda = \int_0^{\infty} r P(r) dr. \quad . \quad . \quad . \quad . \quad (1)$$

$P(r)dr$ may be evaluated very simply by the use of Boltzmann's principle. The work W required to evacuate a spherical volume of radius r is $\rho dr = \frac{4}{3}\pi r^3 \cdot n \cdot RT$. The probability that a sphere of radius r surrounding A contains no other molecules is therefore $e^{-W/RT}$, that is $e^{-\frac{4}{3}\pi r^3 n}$. The differential of this quantity with respect to r and with a minus sign prefixed is obviously that probability that the nearest neighbour of A lies at a distance between r and $r+dr$ from it. Hence $P(r)dr = e^{-\frac{4}{3}\pi r^3 n} \cdot 4\pi r^2 \cdot n dr$.

Multiplying this by r and integrating, we have

$$\lambda = \int_0^{\infty} e^{-\frac{4}{3}\pi r^3 n} \cdot 4\pi r^3 \cdot n dr. \quad . \quad . \quad . \quad . \quad (2)$$

Writing $x = \frac{4}{3}\pi n r^3$, this may be evaluated thus

$$\lambda = \left(\frac{3}{4\pi n}\right)^{1/3} \int_0^{\infty} x^{1/3} e^{-x} dx = \left(\frac{3}{4\pi n}\right)^{1/3} \Gamma\left(\frac{4}{3}\right) = 0.554 n^{-1/3}. \quad . \quad . \quad . \quad . \quad (3)$$

The same result is obtained by Hertz and by Gans in a different way (*loc. cit.*).

An approximate value of λ may be obtained very simply as follows :—The probability that a molecule will be found at a distance between r and $r+dr$ from molecule A is $4\pi r^2 n \cdot dr$. For small values of r we may, without serious error, take the probability of just one molecule being found within a sphere of radius r drawn round A as centre to be simply $\int_0^r 4\pi r^2 n \cdot dr$. The mean distance between A and its neighbour is the radius of the sphere for which this probability is unity. Thus $\lambda = r$, where $\frac{4}{3}\pi n r^3 = 1$.

Hence $\lambda = \left(\frac{3}{4\pi n}\right)^{1/3} = 0.62 n^{-1/3}$, which does not differ very greatly from the accurate value given above.

3. The Case of Dense Fluids.

The preceding discussion makes it clear that for the same density a chaotic distribution of the molecules gives a considerably smaller value for the mean distance between neighbours than a regular ordering in space. According to the thermodynamic theory of density fluctuations in fluids developed by Smoluchowski and Einstein, a highly compressible fluid, *e. g.*, a gas, exhibits greater relative fluctuations of density—that is, greater irregularities in the space-arrangement of the molecules—than a relatively incompressible one, *e. g.*, a liquid at ordinary temperatures and pressures, and the study of the scattering of light and of X-rays in fluids fully substantiates this. Hence, it is seen that, in the formula $\lambda = k \cdot n^{-1/3}$, k should have a larger value for the liquid than for the gaseous state; it may indeed be expected that the value of k in liquids approaches pretty closely the value unity characteristic of a cubical ordering in space.

For dense fluids, as in gases, we have

$$\lambda = \int_0^{\infty} r P(r) dr.$$

The problem is to find the form of the function $P(r)$. If σ be the diameter of a molecule, $P(r)$ obviously vanishes when $r < \sigma$, hence we may write

$$\lambda = \int_{\sigma}^{\infty} r P(r) dr. \quad (4)$$

Let $W(r)$ denote the work required to create a spherical cavity of radius r with the molecule A at its centre. $W(r)$ vanishes when $r = \sigma$. Applying Boltzmann's principle, we have, as before, $P(r) dr = e^{-W(r)/RT} \cdot W'(r)/RT \cdot dr$, and

$$\lambda = \int_{\sigma}^{\infty} r \cdot e^{-\frac{W(r)}{RT}} \cdot W'(r) \cdot \frac{1}{RT} \cdot dr. \quad (5)$$

If we denote the pressure per unit area on the wall of the cavity by $RT\phi(r)$, then

$$W'(r) dr = 4\pi r^2 \cdot RT\phi(r) \cdot dr,$$

and

$$\lambda = \int_{\sigma}^{\infty} e^{-\int_{\sigma}^r 4\pi r'^2 \phi(r') dr'} \cdot 4\pi r^3 \phi(r) dr. \quad (6)$$

The total pressure $4\pi r^2 \cdot \phi(r) \cdot RT$ on the surface of the spherical cavity is obviously due to, (a) the impact of

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the molecules outside the cavity on its boundary, and (b) the resultant of the attractions of the molecules outside the cavity on each other and on the molecule at its centre; in a dense fluid, owing to the proximity of the molecules, these attractions may be very considerable, as is well known. To enable λ to be evaluated, we may as a first approximation take $\phi(r)$ to be equal to a constant Φ . We then write

$$\lambda = \int_0^\infty e^{-\frac{1}{2}\pi r^3 - \sigma^3} \cdot 4\pi r^3 \cdot \Phi \cdot dr \quad . \quad . \quad (7)$$

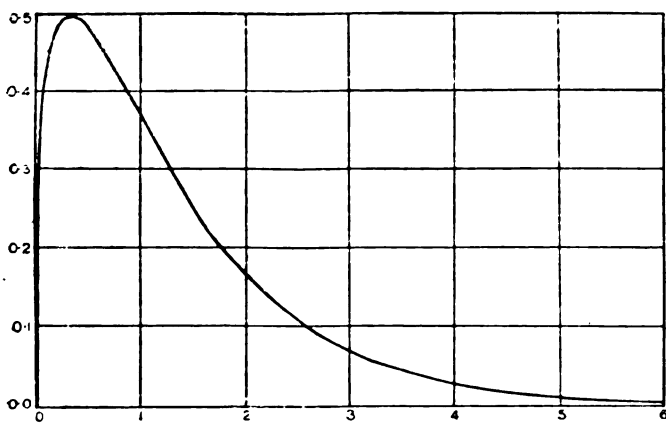
Putting $\frac{1}{2}3\pi r^3 \cdot \Phi = \xi$ and $\frac{1}{2}3\pi\sigma^3 \cdot \Phi = \eta$, we have

$$\lambda = e^\eta \int_\eta^\infty r \cdot e^{-\xi} d\xi = \left(\frac{3}{4\pi\Phi}\right)^{1/3} \cdot e^\eta \int_\eta^\infty \xi^{1/3} \cdot e^{-\xi} d\xi \quad . \quad . \quad (8)$$

$$= \sigma \cdot \frac{e^\eta}{\eta^{1/3}} \int_\eta^\infty \xi^{1/3} e^{-\xi} d\xi \quad . \quad . \quad . \quad (9)$$

The simplest way of evaluating (8) and (9) is by graphical and mechanical integration. The figure gives a graph of

Fig. 1.



Ordinates are $\xi^{1/3} e^{-\xi}$ and Abscissae are ξ

Graph of $\xi^{1/3} e^{-\xi}$ as a function of ξ .

the function under integration between $\xi=0$ and $\xi=6$, from which it is seen that, except for very small values of the argument, the trend of the curve is practically exponential. When $\eta=0$, the integral is simply $\Gamma(4/3)$.

For small values of η , the integral is best determined by

finding the integral $\int_0^\eta \xi^{1/3} e^{-\xi} d\xi$ from the graph by aid of a planimeter and subtracting it from $\Gamma(4/3)$. For large values of η , the integral may be found directly from a graph of the exponential part of the curve drawn on a suitable scale. The table gives the values of λ thus determined for different values of η :—

Table of Mean Distances.

$\frac{4\pi}{3} \sigma^3 \cdot \Phi$	0.0	0.2	0.4	0.6	0.8	1.0	2.0	3.0	4.0	5.0	5.92
$\lambda \cdot \Phi^{1/3} \dots$	0.554	0.618	0.663	0.698	0.735	0.763	0.880	0.970	1.07	1.12	1.17
$\lambda/\sigma \dots\dots$	∞	1.70	1.45	1.34	1.28	1.23	1.13	1.09	1.08	1.07	1.06

For an ideal gas, $\Phi = n$, and we have from the table $\lambda = 0.554 \times n^{-1/3}$ as already found. It is also seen that for increasing values of Φ , λ diminishes at first rather rapidly and later quite slowly as to approach the same value as the molecular diameter σ . How closely the mean distance between neighbouring molecules tends to approach the molecular diameter depends on the value of η , *i.e.*, on $\Phi(r)RT$, which is the pressure per unit area on the walls of a spherical cavity of radius r surrounding a specified molecule. As already remarked, the pressure is determined by the molecular impacts and also by the molecular attractions, and, in view of the uncertainty regarding the actual laws of attraction between molecules in the immediate vicinity of each other, any estimate of the magnitude of Φ is necessarily provisional. In any case, we are probably not very wide of the mark in taking Φ to be generally of the same order of magnitude as n , the number of molecules per unit of volume. If this assumption be justifiable, η is comparable with $\frac{4}{3}\pi\sigma^3 \cdot n$, that is, with eight times the space occupied by the molecular spheres in unit volume: the second horizontal row of figures would give approximately the value of k , where $\lambda = k \cdot n^{-1/3}$. For a closely packed assemblage of spheres, we know independently that $n \cdot \sigma^3 = \sqrt{2}$ and $\frac{4}{3}\pi\sigma^3 \cdot n = \eta = 5.92$, and that $\lambda n^{1/3} = 1.123$, and also that $\lambda/\sigma = 1.00$. These values agree with the corresponding figures given in the table to within a few per cent.

4. An Alternative Method.

The problem may also be dealt with by the aid of Boltzmann's Distribution Law. In an ideal gas, the probability that a molecule will be found within the space between two contiguous concentric spheres of radii r and $r+dr$ respectively is $4\pi r^2 \cdot n \cdot dr$. In a dense fluid, the probability in question is the same, if the centre of the spheres be an arbitrarily chosen geometrical point. If, however, the centre be the instantaneous position of some specified molecule, its presence must influence the distribution of molecules in its immediate neighbourhood. Let $\psi(r)$ be the work necessary to bring two molecules from infinity to a distance r apart. Then the probability of their being found at a distance r apart is less than the probability of their being out of range of each other's action in the ratio $e^{-\psi(r)/RT}$. Thus we are led to modify the expression $4\pi r^2 \cdot n \cdot dr$ and write it in the form $4\pi r^2 n \chi(r) dr$, where $\chi(r)$ as a first approximation may be taken to be $e^{-\psi(r)/RT}$; from the nature of the case it is clear that when $r < \sigma$, $\chi(r)$ vanishes, and that for large values of r , $\chi(r)$ becomes unity.

Considering now a particular molecule, let $P(r) dr$ be the probability that the distance between it and its nearest neighbour is between r and $r+dr$. Then the probability that there are no molecules at a distance between 0 and r

from it is $1 - \int_0^r P(r) dr$. The probability that there is a

molecule between r and $r+dr$ distant from it is $4\pi r^2 \cdot n \cdot \chi(r)$, where $\chi(r)$ is a function of r depending on the intermolecular forces and the density of the fluid as remarked above. We may take the probability that the nearest molecule lies between r and $r+dr$ to be equal to the product of the probabilities that there are no molecules between 0 and r , and that there is one molecule between r and $r+dr$. Therefore

$$\left[1 - \int_0^r P(r) dr\right] 4\pi n r^2 \chi(r) dr = P(r) dr.$$

This is the equation from which we may determine $P(r)$. Differentiating with respect to r , we have

$$\frac{d}{dr} \left[1 - \int_0^r P(r) dr \right] 4\pi n r^2 \chi(r) = - \frac{P(r)}{4\pi r^2 \cdot n \chi(r)} \cdot 4\pi n r^2 \chi(r).$$

Integrating again, we have

$$P(r) = 4\pi r^2 \cdot n \chi(r) \cdot e^{-\int_0^r 4\pi n r^2 \chi(r) dr} \times \text{constant}.$$

The value of the constant of integration is evidently 1, as, when r is small, $P(r) = 4\pi nr^2 \chi(r)$. It follows that

$$\lambda = \int_{\sigma}^{\infty} 4\pi nr^3 \chi(r) \cdot e^{-\int_{\sigma}^r 4\pi nr^2 \chi(r) dr} \cdot dr.$$

It will be noticed that the expression is of the same general form as that obtained previously, and the numerical discussion proceeds on identical lines.

If we make the special assumption that the molecular centres are distributed more or less uniformly in available space, even in the immediate neighbourhood of the specified molecule under consideration, then $\chi(r) = 1$ and

$$\lambda = \int_{\sigma}^{\infty} e^{-4/3\pi n(r^3 - \sigma^3)} \cdot 4\pi n \cdot r^3 \cdot dr. \quad (10)$$

We have already discussed the evaluation of this integral (see (7) above). As in the case of an ideal gas, values of λ agreeing pretty closely with those given by the complete formula may be obtained in the following way. The available space for the centres of other molecules within a sphere of radius r round the centre of a specified molecule is $4/3\pi(r^3 - \sigma^3)$. The probability of a molecule being found within this space is $4/3\pi n \cdot (r^3 - \sigma^3)$. The particular value of r for which this probability is unity gives the mean distance λ between neighbouring molecules. Thus

$$4/3\pi n(\lambda^3 - \sigma^3) = 1 \quad \text{and} \quad \lambda = \left(\frac{3}{4\pi n} + \sigma^3 \right)^{1/3}. \quad (11)$$

For small values of the density, this gives $\lambda = 0.62 \cdot n^{-1/3}$ and for great values of the density $\lambda = \sigma$. The following table shows how closely the values of λ obtained from formulæ (10) and (11) agree with each other:—

Comparison between (10) and (11).

$4/3\pi n \cdot \sigma^3$	0.0	0.2	0.4	0.6	0.8	1.0	2.0	3.0	4.0	5.0	5.92
$\lambda \times n^{1/3}$	(10)	0.554	0.618	0.663	0.698	0.735	0.763	0.880	0.970	1.07	1.17
	(11)	0.620	0.659	0.694	0.725	0.754	0.781	0.894	0.984	1.06	1.13
$\lambda \cdot \sigma$	(10)	∞	1.70	1.45	1.34	1.28	1.23	1.13	1.09	1.08	1.07
	(11)	∞	1.82	1.52	1.38	1.31	1.26	1.14	1.09	1.08	1.06

It will be noted that the rough formula gives practically the same values for λ as the more elaborate calculation.

5. *Remarks on Gans's Paper.*

Finally, a few words will not be out of place regarding the treatment of the problem by R. Gans in the paper already cited. He takes the molecules to be spheres of diameter σ and takes the probability that two molecules will be found at a specified distance r apart to be given by the expression

$$4\pi r^2 \cdot n dr \left[1 + \frac{b}{V} + \frac{5}{8} \left(\frac{b}{V} \right)^2 + 0.287 \left(\frac{b}{V} \right)^3 + \dots \right],$$

where
$$\frac{b}{V} = \frac{2}{3} \pi n \sigma^3.$$

This expression, as is well known, was obtained by Boltzmann, Happel, and others on the assumption that r is practically identical with σ , that is for two molecules in collision, and is inapplicable when $r > \sigma$. Gans also ignores the effect of the van der Waal's attractive or cohesive forces on the relative position of the molecules in space. That this is not justifiable is, *prima facie*, clear from Boltzmann's Distribution Law; that the ordering of the molecules in the space occupied by a fluid is not determined merely by its density as contemplated by Gans is made sufficiently evident by the facts regarding the scattering of light in liquids and in vapours, and especially by the phenomenon of the opalescence which develops as the critical temperature is approached. The discussion given in the foregoing pages indicates that the theory of density-fluctuations in fluids and the problem of the mean distance between neighbouring molecules are closely related to each other.

6. *Summary and Conclusion.*

(a) The paper considers the problem of determining the mean distance in question by two distinct methods. In the first, Boltzmann's thermodynamic principle of Entropy-Probability is applied, and the chance that the nearest neighbour of a given molecule is situated at a specified distance from it is expressed in terms of the work done in creating a spherical cavity round the molecule in question. In the second method, Boltzmann's Distribution Law for the molecular positions in space is employed. Expressions

for the mean distance which are formally analogous are given by the two methods.

(b) The mean distance λ between neighbouring molecules is given by the formula $k \cdot n^{-1/3}$, where n is the number of molecules in unit volume and k is a fraction which varies from 0.554 for an ideal gas up to 1.12 for the closest packing. The value of k for actual liquids may range from about 0.8 to 1.0. For dense fluids, λ is of the same order of quantities as the molecular diameter, but may be 10 per cent. to 20 per cent. greater.

(c) Tolerably accurate values of λ may be obtained by a very simple mathematical treatment.

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Calcutta,
October 10, 1923.

LXII. *Certain Types of Elastic Stress which are peculiarly related to each of the several Curvilinear Orthogonal Coordinate Systems.* By R. F. GWYTHER, M.A.*

IN a paper † dealing with the Stress Equations referred to general orthogonal coordinates, I have shown that the six elements of stress can be expressed in either of two forms (the θ -form and the ψ -form) in terms of three general and arbitrary functions.

In this paper I propose to make use of the values of the stresses in the θ -form to investigate the conditions under which, when the stresses are elastic, the components of the displacement can be expressed in terms of the same three functions as the stresses, and to continue the discussion in the simpler of the cases concerned.

1. The values of S, T, U given in the paper just referred to are :—

$$\begin{aligned} S &= h_2 h_3 \frac{\partial^2 \theta_1}{\partial \eta \partial \zeta} + \left(h_3 \frac{\partial h_2}{\partial \zeta} - \frac{h_2 h_3}{h_1} \frac{\partial h_1}{\partial \zeta} \right) \frac{\partial \theta_1}{\partial \eta} \\ &\quad + \left(h_2 \frac{\partial h_3}{\partial \eta} - \frac{h_2 h_3}{h_1} \frac{\partial h_1}{\partial \eta} \right) \frac{\partial \theta_1}{\partial \zeta}, \\ T &= \frac{h_1 h_3}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial \theta_1}{\partial \zeta}, \\ U &= \frac{h_1 h_2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial \theta_1}{\partial \eta}. \end{aligned} \quad \dots \dots \dots (1)$$

as far as θ_1 and its differential coefficients are concerned.

* Communicated by the Author.

† Phil. Mag. September 1923, p. 481.

The values are ultimately to be completed by a process of cyclical interchange, so as to include the terms in θ_2 and θ_3 . Writing the components of the displacement as u , v , w , the necessary conditions include

$$\begin{aligned} S = na &= n \left\{ \frac{h_2}{h_3} \frac{\partial(h_3 w)}{\partial \eta} + \frac{h_3}{h_2} \frac{\partial(h_2 v)}{\partial \xi} \right\}, \\ T = nb &= n \left\{ \frac{h_3}{h_1} \frac{\partial(h_1 u)}{\partial \xi} + \frac{h_1}{h_3} \frac{\partial(h_3 w)}{\partial \xi} \right\}, \\ U = nc &= n \left\{ \frac{h_1}{h_2} \frac{\partial(h_2 v)}{\partial \xi} + \frac{h_2}{h_1} \frac{\partial(h_1 u)}{\partial \eta} \right\}. \quad (2) \end{aligned}$$

There is only one case in which these conditions can be satisfied absolutely, which is when

$$\begin{aligned} &\text{and} \quad \theta_1 = \theta_2 = \theta_3 = \phi, \\ 2nu &= h_1 \frac{\partial \phi}{\partial \xi}, \quad 2nv = h_2 \frac{\partial \phi}{\partial \eta}, \quad 2nw = h_3 \frac{\partial \phi}{\partial \xi}. \quad (3) \end{aligned}$$

In the general case, which will be contingent, the mode in which the differential coefficients of the θ 's enter the values of the components of the displacement are fairly obvious, and must reduce to those in (3), when the θ 's are all made equal.

We therefore shall write in the most general case :

$$\begin{aligned} 2nu &= h_1 \frac{\partial}{\partial \xi} (\theta_2 + \theta_3 - \theta_1) + \alpha_3 (\theta_3 - \theta_1) - \alpha_2 (\theta_1 - \theta_2), \\ 2nv &= h_2 \frac{\partial}{\partial \eta} (\theta_3 + \theta_1 - \theta_2) + \beta_1 (\theta_1 - \theta_2) - \beta_3 (\theta_2 - \theta_3), \\ 2nw &= h_3 \frac{\partial}{\partial \xi} (\theta_1 + \theta_2 - \theta_3) + \gamma_2 (\theta_2 - \theta_3) - \gamma_1 (\theta_3 - \theta_1), \quad (4) \end{aligned}$$

in which a cyclical symmetry is effected.

On substitution, the first of the conditions (2) becomes

$$\begin{aligned} 0 &= \left(\frac{\beta_1}{h_2} + \frac{2}{h_1} \frac{\partial h_1}{\partial \eta} \right) \frac{\partial(\theta_1 - \theta_2)}{\partial \xi} - \left(\frac{\gamma_1}{h_3} + \frac{2}{h_1} \frac{\partial h_1}{\partial \xi} \right) \frac{\partial(\theta_3 - \theta_1)}{\partial \eta} \\ &\quad + \left(\frac{\gamma_2}{h_3} - \frac{2}{h_2} \frac{\partial h_2}{\partial \xi} \right) \frac{\partial(\theta_2 - \theta_3)}{\partial \eta} - \left(\frac{\beta_3}{h_2} - \frac{2}{h_3} \frac{\partial h_3}{\partial \eta} \right) \frac{\partial(\theta_2 - \theta_3)}{\partial \xi} \\ &\quad + \frac{1}{h_2^2} \frac{\partial(h_2 \beta_1)}{\partial \xi} (\theta_1 - \theta_2) - \frac{1}{h_3^2} \frac{\partial(h_3 \gamma_1)}{\partial \eta} (\theta_3 - \theta_1) \\ &\quad + \left\{ \frac{1}{h_3^2} \frac{\partial(h_3 \gamma_2)}{\partial \eta} - \frac{1}{h_2^2} \frac{\partial(h_2 \beta_3)}{\partial \xi} \right\} (\theta_2 - \theta_3) \quad (5) \end{aligned}$$

The other two equations of condition may be written down by a process of cyclical interchange.

2. The three conditions for elastic equilibrium which I shall select for preliminary consideration are no doubt simpler than the remaining three, and my next step will be to simplify the form of the conditions expressed in (5) by the selection of values for the six arbitrary constants contained in them. The selection decided upon must find its support in the sequel.

The choice made is that the coefficients of $\partial(\theta_1 - \theta_2)/\partial\zeta$, $\partial(\theta_3 - \theta_1)/\partial\eta$, and of similar terms in the other equations shall be made null; that is, I make

$$\begin{aligned}\beta_1 &= -2\frac{h_2}{h_1} \frac{\partial h_1}{\partial\eta}; & \gamma_2 &= -2\frac{h_3}{h_2} \frac{\partial h_2}{\partial\zeta}; & \alpha_3 &= -2\frac{h_1}{h_3} \frac{\partial h_3}{\partial\xi}; \\ \gamma_1 &= -2\frac{h_3}{h_1} \frac{\partial h_1}{\partial\zeta}; & \alpha_2 &= -2\frac{h_1}{h_2} \frac{\partial h_2}{\partial\xi}; & \beta_3 &= -2\frac{h_2}{h_3} \frac{\partial h_3}{\partial\eta}.\end{aligned}\quad (6)$$

The first of the conditions (5) thus becomes

$$\begin{aligned}& 2\left(\frac{1}{h_3} \frac{\partial h_3}{\partial\eta} \frac{\partial}{\partial\zeta} - \frac{1}{h_2} \frac{\partial h_2}{\partial\zeta} \frac{\partial}{\partial\eta}\right)(\theta_2 - \theta_3) \\ & - \frac{1}{h_2^2} \frac{\partial}{\partial\zeta} \left(\frac{h_2^2}{h_1} \frac{\partial h_1}{\partial\eta}\right)(\theta_1 - \theta_2) + \frac{1}{h_3^2} \frac{\partial}{\partial\eta} \left(\frac{h_3^2}{h_1} \frac{\partial h_1}{\partial\zeta}\right)(\theta_3 - \theta_1) \\ & + \left\{ \frac{1}{h_2^2} \frac{\partial}{\partial\zeta} \left(\frac{h_2^2}{h_3} \frac{\partial h_3}{\partial\eta}\right) - \frac{1}{h_3^2} \frac{\partial}{\partial\eta} \left(\frac{h_3^2}{h_2} \frac{\partial h_2}{\partial\zeta}\right) \right\} (\theta_2 - \theta_3) = 0.\end{aligned}\quad (7)$$

By the use of Lamé's Identities, quoted in the paper previously referred to, this may be written

$$\begin{aligned}& 2\left(h_2 \frac{\partial h_3}{\partial\eta} \frac{\partial}{\partial\zeta} - h_3 \frac{\partial h_2}{\partial\zeta} \frac{\partial}{\partial\eta}\right)(\theta_2 - \theta_3) - \frac{h_2 h_3}{h_1^2} \frac{\partial h_1}{\partial\eta} \frac{\partial h_1}{\partial\zeta} (2\rho_1 - \theta_2 - \theta_3) \\ & + \left\{ h_2 \frac{\partial^2 h_3}{\partial\eta \partial\zeta} - h_3 \frac{\partial^2 h_2}{\partial\eta \partial\zeta} + \frac{h_3}{h_2} \frac{\partial h_2}{\partial\eta} \frac{\partial h_2}{\partial\zeta} - \frac{h_2}{h_3} \frac{\partial h_3}{\partial\eta} \frac{\partial h_3}{\partial\zeta} \right. \\ & \left. + \frac{h_3}{h_1} \frac{\partial h_1}{\partial\eta} \frac{\partial h_2}{\partial\zeta} - \frac{h_2}{h_1} \frac{\partial h_1}{\partial\zeta} \frac{\partial h_3}{\partial\eta} \right\} (\theta_2 - \theta_3) = 0,\end{aligned}\quad (8)$$

with two homologous equations.

These give relations between the differences of the three functions on which the stress-system depends and the particular orthogonal coordinate system to which the stress-system is referred.

The value of e is given

$$e = h_1 \frac{\partial u}{\partial \xi} - \frac{h_2}{h_1} \frac{\partial h_1}{\partial \eta} v - \frac{h_3}{h_1} \frac{\partial h_1}{\partial \zeta} w,$$

and there are homologous expressions for f and g , in which we are to substitute for u , v , w from (9).

Thus we find

$$\begin{aligned} 2ne = & -h_1^2 \frac{\partial^2 \theta_1}{\partial \xi^2} - \left(h_1 \frac{\partial h_1}{\partial \xi} - 2 \frac{h_1^2}{h_2} \frac{\partial h_2}{\partial \xi} - 2 \frac{h_1^2}{h_3} \frac{\partial h_3}{\partial \xi} \right) \frac{\partial \theta_1}{\partial \xi} \\ & - \frac{h_2^2}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial \theta_1}{\partial \eta} - \frac{h_3^2}{h_1} \frac{\partial h_1}{\partial \zeta} \frac{\partial \theta_1}{\partial \zeta} \\ & + 2\theta_1 \left\{ \frac{h_1^2}{h_2} \frac{\partial^2 h_2}{\partial \xi^2} + \frac{h_1^2}{h_3} \frac{\partial^2 h_3}{\partial \xi^2} + \left(\frac{h_1}{h_2} \frac{\partial h_1}{\partial \xi} - \frac{h_1^2}{h_2^2} \frac{\partial h_2}{\partial \xi} \right) \frac{\partial h_2}{\partial \xi} \right. \\ & \left. + \left(\frac{h_1}{h_3} \frac{\partial h_1}{\partial \xi} - \frac{h_1^2}{h_3^2} \frac{\partial h_3}{\partial \xi} \right) \frac{\partial h_3}{\partial \xi} + \frac{h_2^2}{h_1^2} \left(\frac{\partial h_1}{\partial \eta} \right)^2 + \frac{h_3^2}{h_1^2} \left(\frac{\partial h_1}{\partial \zeta} \right)^2 \right\}, \\ 2nf = & h_2^2 \frac{\partial^2 \theta_1}{\partial \eta^2} + \frac{h_1^2}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial \theta_1}{\partial \xi} + \left(h_2 \frac{\partial h_2}{\partial \eta} - 2 \frac{h_2^2}{h_1} \frac{\partial h_1}{\partial \eta} \right) \frac{\partial \theta_1}{\partial \eta} - \frac{h_3^2}{h_2} \frac{\partial h_2}{\partial \zeta} \frac{\partial \theta_1}{\partial \zeta} \\ & - 2\theta_1 \left\{ \frac{h_2^2}{h_1} \frac{\partial^2 h_1}{\partial \eta^2} + \left(\frac{h_2}{h_1} \frac{\partial h_2}{\partial \eta} - \frac{h_2^2}{h_1^2} \frac{\partial h_1}{\partial \eta} \right) \frac{\partial h_1}{\partial \eta} \right. \\ & \left. + \left(\frac{h_1^2}{h_2^2} \frac{\partial h_2}{\partial \xi} + \frac{h_1^2}{h_2 h_3} \frac{\partial h_3}{\partial \xi} \right) \frac{\partial h_2}{\partial \xi} - \frac{h_3^2}{h_1 h_2} \frac{\partial h_1}{\partial \zeta} \frac{\partial h_2}{\partial \zeta} \right\}, \\ 2ng = & h_3^2 \frac{\partial^2 \theta_1}{\partial \zeta^2} + \frac{h_1^2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial \theta_1}{\partial \xi} - \frac{h_2^2}{h_3} \frac{\partial h_3}{\partial \eta} \frac{\partial \theta_1}{\partial \eta} + \left(h_3 \frac{\partial h_3}{\partial \zeta} - 2 \frac{h_3^2}{h_1} \frac{\partial h_1}{\partial \zeta} \right) \frac{\partial \theta_1}{\partial \zeta} \\ & - 2\theta_1 \left\{ \frac{h_3^2}{h_1} \frac{\partial^2 h_1}{\partial \zeta^2} + \left(\frac{h_3}{h_1} \frac{\partial h_3}{\partial \zeta} - \frac{h_3^2}{h_1^2} \frac{\partial h_1}{\partial \zeta} \right) \frac{\partial h_1}{\partial \zeta} \right. \\ & \left. + \left(\frac{h_1^2}{h_3^2} \frac{\partial h_3}{\partial \xi} + \frac{h_1^2}{h_2 h_3} \frac{\partial h_2}{\partial \xi} \right) \frac{\partial h_3}{\partial \xi} - \frac{h_2^2}{h_1 h_3} \frac{\partial h_1}{\partial \eta} \frac{\partial h_3}{\partial \eta} \right\}. \quad (12) \end{aligned}$$

as far as θ_1 is concerned.

Combining these values with those given for P , Q , R in (10), and using Lamé's Identities, the simplifications are notable, and we find

$$P - Q - 2n(e - f) = \nabla^2 \theta_1 - 2\theta_1 \left\{ 2 \frac{h_2^2}{h_1^2} \left(\frac{\partial h_1}{\partial \eta} \right)^2 + 2 \frac{h_1^2}{h_3^2} \left(\frac{\partial h_2}{\partial \xi} \right)^2 \right. \\ \left. + \frac{h_3^2}{h_1^2} \left(\frac{\partial h_1}{\partial \zeta} \right)^2 + \frac{h_1^2}{h_3^2} \left(\frac{\partial h_3}{\partial \xi} \right)^2 \right\},$$

$$R - P - 2n(g - e) = -\nabla^2 \theta_1 + 2\theta_1 \left\{ \frac{h_2^2}{h_1^2} \left(\frac{\partial h_1}{\partial \eta} \right)^2 + \frac{h_1^2}{h_2^2} \left(\frac{\partial h_2}{\partial \xi} \right)^2 \right. \\ \left. + 2 \frac{h_3^2}{h_1^2} \left(\frac{\partial h_1}{\partial \zeta} \right)^2 + 2 \frac{h_1^2}{h_3^2} \left(\frac{\partial h_3}{\partial \xi} \right)^2 \right\}.$$

whence

$$Q - R - 2n(f - g) = 2\theta_1 \left\{ \frac{h_2^2}{h_1^2} \left(\frac{\partial h_1}{\partial \eta} \right)^2 + \frac{h_1^2}{h_2^2} \left(\frac{\partial h_2}{\partial \xi} \right)^2 - \frac{h_3^2}{h_1^2} \left(\frac{\partial h_1}{\partial \xi} \right)^2 - \frac{h_1^2}{h_3^2} \left(\frac{\partial h_3}{\partial \xi} \right)^2 \right\} \dots \quad (13)$$

By completing $P - Q - 2n(e - f)$ so as to include terms in θ_2 and θ_3 , we find

$$\begin{aligned} \nabla^2(\theta_1 - \theta_2) - 4(\theta_1 - \theta_2) \left\{ \frac{h_2^2}{h_1^2} \left(\frac{\partial h_1}{\partial \eta} \right)^2 + \frac{h_1^2}{h_2^2} \left(\frac{\partial h_2}{\partial \xi} \right)^2 \right\} \\ + 2(\theta_2 - \theta_3) \left\{ \frac{h_3^2}{h_2^2} \left(\frac{\partial h_2}{\partial \xi} \right)^2 + \frac{h_2^2}{h_3^2} \left(\frac{\partial h_3}{\partial \eta} \right)^2 \right\} \\ + 2(\theta_3 - \theta_1) \left\{ \frac{h_3^2}{h_2^2} \left(\frac{\partial h_1}{\partial \xi} \right)^2 + \frac{h_1^2}{h_3^2} \left(\frac{\partial h_3}{\partial \xi} \right)^2 \right\} = 0 \end{aligned}$$

with homologous equations. . . (14)

4. The last condition to be satisfied is

$$P + Q + R = (3m - n)(e + f + g).$$

We find from (11) that

$$\begin{aligned} P + Q + R \\ = -\nabla^2(\theta_1 + \theta_2 + \theta_3) + h_1 h_2 h_3 \left\{ \frac{\partial}{\partial \xi} \left(\frac{h_1}{h_2 h_3} \frac{\partial \theta_1}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(\frac{h_2}{h_3 h_1} \frac{\partial \theta_2}{\partial \eta} \right) \right. \\ \left. + \frac{\partial}{\partial \xi} \left(\frac{h_3}{h_1 h_2} \frac{\partial \theta_3}{\partial \xi} \right) \right\} \\ - \left(\frac{h_1^2}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial}{\partial \xi} - \frac{h_2^2}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial}{\partial \eta} \right) (\theta_1 - \theta_2) \\ - \left(\frac{h_2^2}{h_3} \frac{\partial h_3}{\partial \eta} \frac{\partial}{\partial \eta} - \frac{h_3^2}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial}{\partial \xi} \right) (\theta_2 - \theta_3) \\ - \left(\frac{h_3^2}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial}{\partial \xi} - \frac{h_1^2}{h_3} \frac{\partial h_3}{\partial \eta} \frac{\partial}{\partial \eta} \right) (\theta_3 - \theta_1) \\ + 2A_1\theta_1 + 2A_2\theta_2 + 2A_3\theta_3 \dots \dots \dots (15) \end{aligned}$$

where

$$\begin{aligned} A_1 = \frac{h_2^2}{h_1} \frac{\partial^2 h_1}{\partial \eta^2} - 2 \frac{h_2^2}{h_1^2} \left(\frac{\partial h_1}{\partial \eta} \right)^2 + \frac{h_2}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial h_2}{\partial \eta} - \frac{h_2^2}{h_1 h_3} \frac{\partial h_1}{\partial \eta} \frac{\partial h_3}{\partial \eta} \\ + \frac{h_3^2}{h_1} \frac{\partial^2 h_1}{\partial \xi^2} - 2 \frac{h_3^2}{h_1^2} \left(\frac{\partial h_1}{\partial \xi} \right)^2 - \frac{h_3^2}{h_1 h_2} \frac{\partial h_1}{\partial \xi} \frac{\partial h_2}{\partial \xi} + \frac{h_3}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_3}{\partial \xi} \\ + \frac{h_1^2}{h_2 h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \xi}, \end{aligned}$$

or

$$= - \left\{ \frac{h_1^2}{h_2} \frac{\partial^2 h_2}{\partial \xi^2} + \frac{h_1}{h_2} \frac{\partial h_1}{\partial \xi} \frac{\partial h_2}{\partial \xi} - 2 \frac{h_1^2}{h_2^2} \left(\frac{\partial h_2}{\partial \xi} \right)^2 \right. \\ \left. + \frac{h_1^2}{h_3} \frac{\partial^2 h_3}{\partial \xi^2} + \frac{h_1}{h_3} \frac{\partial h_1}{\partial \xi} \frac{\partial h_3}{\partial \xi} - 2 \frac{h_1^2}{h_3^2} \left(\frac{\partial h_3}{\partial \xi} \right)^2 - \frac{h_1^2}{h_2 h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \xi} \right\},$$

by Lamé's Identities.

By adding these two values is found the value of $2A_1$ in the form presenting itself in the next paragraph.

The expressions for A_2 and A_3 are homologous to that for A_1 .

Similarly, we find from (12) :

$$2n(e+f+g) \\ = \nabla^2(\theta_1 + \theta_2 + \theta_3) - 2h_1 h_2 h_3 \left\{ \frac{\partial}{\partial \xi} \left(\frac{h_1}{h_2 h_3} \frac{\partial \theta_1}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(\frac{h_2}{h_3 h_1} \frac{\partial \theta_2}{\partial \eta} \right) \right. \\ \left. + \frac{\partial}{\partial \zeta} \left(\frac{h_3}{h_1 h_2} \frac{\partial \theta_3}{\partial \zeta} \right) \right\} \\ + 2 \left(\frac{h_1^2}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial}{\partial \xi} - \frac{h_2^2}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial}{\partial \eta} \right) (\theta_1 - \theta_2) \\ + 2 \left(\frac{h_2^2}{h_3} \frac{\partial h_3}{\partial \eta} \frac{\partial}{\partial \eta} - \frac{h_3^2}{h_2} \frac{\partial h_2}{\partial \zeta} \frac{\partial}{\partial \zeta} \right) (\theta_2 - \theta_3) \\ + 2 \left(\frac{h_3^2}{h_1} \frac{\partial h_1}{\partial \zeta} \frac{\partial}{\partial \zeta} - \frac{h_1^2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial}{\partial \xi} \right) (\theta_3 - \theta_1) \\ - 4A_1 \theta_1 - 4A_2 \theta_2 - 4A_3 \theta_3. \quad \dots \quad (16).$$

The condition which we seek therefore becomes

$$(3m+n) \nabla^2(\theta_1 + \theta_2 + \theta_3) \\ = 6m \left[h_1 h_2 h_3 \left\{ \frac{\partial}{\partial \xi} \left(\frac{h_1}{h_2 h_3} \frac{\partial \theta_1}{\partial \xi} \right) + \frac{\partial}{\partial \eta} \left(\frac{h_2}{h_3 h_1} \frac{\partial \theta_2}{\partial \eta} \right) + \frac{\partial}{\partial \zeta} \left(\frac{h_3}{h_1 h_2} \frac{\partial \theta_3}{\partial \zeta} \right) \right\} \right. \\ - \left(\frac{h_1^2}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial}{\partial \xi} - \frac{h_2^2}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial}{\partial \eta} \right) (\theta_1 - \theta_2) \\ - \left(\frac{h_2^2}{h_3} \frac{\partial h_3}{\partial \eta} \frac{\partial}{\partial \eta} - \frac{h_3^2}{h_2} \frac{\partial h_2}{\partial \zeta} \frac{\partial}{\partial \zeta} \right) (\theta_2 - \theta_3) \\ - \left(\frac{h_3^2}{h_1} \frac{\partial h_1}{\partial \zeta} \frac{\partial}{\partial \zeta} - \frac{h_1^2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial}{\partial \xi} \right) (\theta_3 - \theta_1) \\ \left. + 2A_1 \theta_1 + 2A_2 \theta_2 + 2A_3 \theta_3 \right] \quad \dots \quad (17).$$

If we write.

$$2A_1 = 2 \frac{h_1^2}{h_2 h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \xi} + B_3 - B_2,$$

where

$$B_3 = \frac{h_2^2}{h_1^2} \frac{\partial^2 h_1}{\partial \eta^2} - \frac{h_1^2}{h_2} \frac{\partial h_2}{\partial \xi^2} - 2 \frac{h_2^2}{h_1^2} \left(\frac{\partial h_1}{\partial \eta} \right)^2 + 2 \frac{h_1^2}{h_2^2} \left(\frac{\partial h_2}{\partial \xi} \right)^2 \\ + \frac{h_2}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial h_2}{\partial \eta} - \frac{h_1}{h_2} \frac{\partial h_1}{\partial \xi} \frac{\partial h_2}{\partial \xi} - \frac{h_3^2}{h_1 h_2} \frac{\partial h_1}{\partial \xi} \frac{\partial h_2}{\partial \xi},$$

$$B_2 = \frac{h_1^2}{h_3} \frac{\partial^2 h_3}{\partial \xi^2} - \frac{h_3}{h_1} \frac{\partial h_1}{\partial \xi^2} - 2 \frac{h_1^2}{h_3^2} \left(\frac{\partial h_3}{\partial \xi} \right)^2 + 2 \frac{h_3^2}{h_1^2} \left(\frac{\partial h_1}{\partial \xi} \right)^2 \\ + \frac{h_1}{h_3} \frac{\partial h_1}{\partial \xi} \frac{\partial h_3}{\partial \xi} - \frac{h_3}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_3}{\partial \xi} - \frac{h_2^2}{h_1 h_3} \frac{\partial h_1}{\partial \eta} \frac{\partial h_3}{\partial \eta},$$

with similar expressions for $2A_2$ and $2A_3$,

we shall find

$$2A_1 \theta_1 + 2A_2 \theta_2 + 2A_3 \theta_3 \\ = 2 \frac{h_1^2}{h_2 h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \xi} \theta_1 + 2 \frac{h_2^2}{h_1 h_3} \frac{\partial h_1}{\partial \eta} \frac{\partial h_3}{\partial \eta} \theta_2 + 2 \frac{h_3^2}{h_1 h_2} \frac{\partial h_1}{\partial \xi} \frac{\partial h_2}{\partial \xi} \theta_3 \\ + B_1(\theta_2 - \theta_3) + B_2(\theta_3 - \theta_1) + B_3(\theta_1 - \theta_2),$$

for substitution in (17) if desired.

5. For a complete exposition, it would be necessary to employ the expressions for u, v, w given in (4) to find e, f, g , and repeat the procedure in sections 3 and 4,—the constants taking finally values selected from

$$\beta_1 = \pm \frac{2h_2}{h_1} \frac{\partial h_1}{\partial \eta}, \quad \gamma_2 = \pm 2 \frac{h_3}{h_2} \frac{\partial h_2}{\partial \xi}, \quad \alpha_3 = \pm 2 \frac{h_1}{h_2} \frac{\partial h_3}{\partial \xi}, \\ \gamma_1 = \pm \frac{2h_3}{h_1} \frac{\partial h_1}{\partial \xi}, \quad \alpha_2 = \pm 2 \frac{h_1}{h_2} \frac{\partial h_2}{\partial \xi}, \quad \beta_2 = \pm 2 \frac{h_2}{h_3} \frac{\partial h_3}{\partial \eta}.$$

As the results would meet contingencies, they would be valuable, but the process would be lengthy, and I have confined myself to one instance only, in which, however, the general method is fully exemplified.

The interest in general problems in orthogonal coordinate systems turns ultimately upon their application to the simpler of such systems, and I conclude by considering a few cases by the method of this paper. In all such cases I shall retain the coordinates ξ, η, ζ in the sense of the coordinates of the system.

I. *The cylindrical polar system.*

In this case we have

$$h_1 = 1, \quad h_2 = \frac{1}{\xi}, \quad h_3 = 1,$$

so that α_2 is the only remaining constant.

The equations (5) reduce to

$$\left(\alpha_2 - \frac{2}{\xi}\right) \frac{\partial(\theta_1 - \theta_2)}{\partial \xi} = 0, \quad \left(\alpha_2 + \frac{2}{\xi}\right) \frac{\partial(\theta_1 - \theta_2)}{\partial \eta} = 0.$$

The case which I have considered and to which equations (14) and (17) apply is when $\alpha_2 = 2/\xi$ and the condition becomes

$$\frac{\partial(\theta_1 - \theta_2)}{\partial \eta} = 0.$$

There is another case which I have not considered when $\alpha_2 = -2/\xi$ and the condition becomes

$$\frac{\partial(\theta_1 - \theta_2)}{\partial \xi} = 0.$$

II. *The conjugate cylindric system.*

In this case

$$h_1 = h_2 = h = f(\xi, \eta), \quad h_3 = 1,$$

and β_1 and α_2 are the only remaining constants.

The equations (5) now reduce to

$$\left(\beta_1 + 2 \frac{\partial h}{\partial \eta}\right) \frac{\partial(\theta_1 - \theta_2)}{\partial \xi} = 0,$$

$$\left(\alpha_2 + 2 \frac{\partial h}{\partial \xi}\right) \frac{\partial(\theta_1 - \theta_2)}{\partial \xi} = 0,$$

$$\left(\beta_1 - 2 \frac{\partial h}{\partial \eta}\right) \frac{\partial(\theta_1 - \theta_2)}{\partial \xi} - \left(\alpha_2 - 2 \frac{\partial h}{\partial \xi}\right) \frac{\partial(\theta_1 - \theta_2)}{\partial \eta} = 0.$$

The case which has been considered is when $\beta_1 = -2 \frac{\partial h}{\partial \eta}$, $\alpha_2 = -2 \frac{\partial h}{\partial \xi}$, and then the condition is

$$\frac{\partial(\theta_1 - \theta_2)}{\partial \xi} \frac{\partial h}{\partial \eta} - \frac{\partial(\theta_1 - \theta_2)}{\partial \eta} \frac{\partial h}{\partial \xi} = 0,$$

or

$$\theta_1 - \theta_2 = f(h, \xi).$$

Alternatively, if either $\beta_1 = 2 \frac{\partial h}{\partial \eta}$ or $\alpha_2 = 2 \frac{\partial h}{\partial \xi}$, we have

$$\frac{\partial(\theta_1 - \theta_2)}{\partial \xi} = 0, \quad \theta_1 - \theta_2 = f(\xi, \eta).$$

If both $\beta_1 = 2 \frac{\partial h}{\partial \eta}$ and $\alpha_2 = 2 \frac{\partial h}{\partial \xi}$, this is the sole condition ; otherwise $\theta_1 - \theta_2$ is a function either of ξ or of η .

III. The spherical polar system.

Here we have

$$h_1 = 1, \quad h_2 = \frac{1}{\xi}, \quad h_3 = \frac{1}{\xi \sin \eta}.$$

and α_2 , α_3 , and β_3 are the remaining constants.

The equations (5) become

$$\begin{aligned} & \left(\beta_3 - \frac{2}{h_3} \frac{\partial h_3}{\partial \eta} \right) \frac{\partial(\theta_2 - \theta_1)}{\partial \xi} = 0, \\ & \left(\frac{\alpha_2}{h_1} + \frac{2}{h_2} \frac{\partial h_2}{\partial \xi} \right) \frac{\partial(\theta_1 - \theta_2)}{\partial \xi} - \left(\frac{\alpha_3}{h_1} - \frac{2}{h_3} \frac{\partial h_3}{\partial \xi} \right) \frac{\partial(\theta_3 - \theta_1)}{\partial \xi} = 0, \\ & \left(\frac{\alpha_3}{h_1} + \frac{2}{h_3} \frac{\partial h_3}{\partial \xi} \right) \frac{\partial(\theta_3 - \theta_1)}{\partial \eta} - \left(\frac{\beta_3}{h_2} + \frac{2}{h_3} \frac{\partial h_3}{\partial \eta} \right) \frac{\partial(\theta_2 - \theta_3)}{\partial \xi} \\ & \quad - \left(\frac{\alpha_2}{h_1} - \frac{2}{h_2} \frac{\partial h_2}{\partial \xi} \right) \frac{\partial(\theta_1 - \theta_2)}{\partial \eta} + \frac{1}{h_1^2} \frac{\partial(h_1 \alpha_3)}{\partial \eta} (\theta_3 - \theta_1) \\ & \quad - \frac{1}{h_2^2} \frac{\partial(h_2 \beta_3)}{\partial \xi} (\theta_2 - \theta_3) - \frac{1}{h_1^2} \frac{\partial(h_1 \alpha_2)}{\partial \eta} (\theta_1 - \theta_2) = 0. \end{aligned}$$

The values we are to take for α_2 , α_3 , β_3 are :

$$\alpha_2 = \mp 2 \frac{h_1}{h_2} \frac{\partial h_2}{\partial \xi} = \pm \frac{2}{\xi},$$

$$\alpha_3 = \mp 2 \frac{h_1}{h_3} \frac{\partial h_3}{\partial \xi} = \pm \frac{2}{\xi},$$

$$\beta_3 = \mp 2 \frac{h_2}{h_3} \frac{\partial h_3}{\partial \eta} = \pm \frac{2 \cot \eta}{\xi},$$

whence

$$\partial(h_1 \alpha_3) / \partial \eta = 0, \quad \partial(h_1 \alpha_2) / \partial \eta = 0.$$

In the case we have considered, the upper signs are to be

taken and the conditions become

$$\begin{aligned}\frac{\partial(\theta_2 - \theta_3)}{\partial \xi} &= 0, & \frac{\partial(\theta_3 - \theta_1)}{\partial \xi} &= 0, \\ \frac{\partial(\theta_1 - \theta_2)}{\partial \eta} - \cot \eta (\theta_2 - \theta_3) &= 0.\end{aligned}$$

None of the other cases have been considered.

We may describe the conditions (5) as expressing the antecedent condition that the characteristics of the stress system and of the coordinate system are not such as exclude the possibility of the elastic displacement being expressed in terms of the same three functions as the stress, the final conditions being expressed in (14) and (17).

LXIII. *The Emission from an Incandescent Platinum Wire in Air.* By Prof. A. M. TYNDALL, D.Sc., and G. C. GRINDLEY, B.Sc. (*Bristol*) *.

IT is well known that the mobility of the normal ions produced by the usual ionizing agencies in fairly dry dust-free air at atmospheric pressure is of the order of 1.8 cm./sec./volt/cm. for negative and 1.4 for positive ions. An apparent exception to this was found by McClelland † in the case of ions from an incandescent wire, an arc, or a flame. In his experiments an air current carried the ions into a metal tube, in which their mobility was determined by a method which Rutherford had used in the case of ions produced by uranium.

In the case of an incandescent wire, with which the present paper is concerned, McClelland found that the ionic mobility was small compared with that produced by X-rays, and that the hotter the wire the smaller was the mobility. Further the mobility, which was of the order of 0.01 to 0.03 cm./sec., decreased with increase of distance from the source. McClelland concluded that each ion picked up molecules and formed a cluster which grew in size with age. Again, Rutherford ‡ made observations on the current between two plates, one of which was red hot; he concluded that the mobility of the positive ions from platinum may

* Communicated by the Authors.

† McClelland, *Proc. Camb. Phil. Soc.* x, p. 241 (1899).

‡ Rutherford, *Phys. Rev.* xiii, p. 321 (1901).

vary within wide limits, its average value decreasing with increasing distance between the plates.

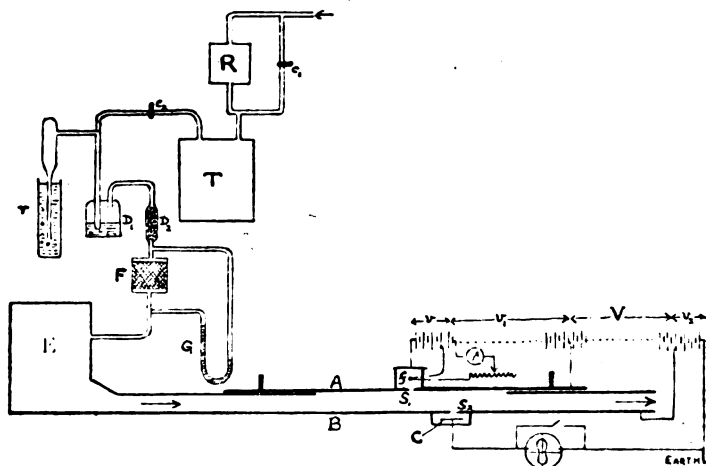
On general grounds it seemed probable that McClelland was dealing with a mixture of different types of ion, the relative proportions of which changed with time. For instance, several writers have referred to the particles of sputtered metal as nuclei to which some ions would attach themselves. The purpose of the following experiments was to obtain more definite information on the whole subject by means of mobility measurements.

Two types of apparatus were used: the first was suggested by an experiment of Nolan* (though differing from it in several respects), and is referred to below as the Box Method; the second was McClelland's original method with modifications.

Box Method.

A sketch of the apparatus is given in fig. 1.

Fig. 1.



A and B, the former in two parts, are brass sheets forming the top and bottom of a rectangular box 72 in. long and 10 in. wide. Except for the insertion of a glass window for observational purposes, the sides of the box were of ebonite about 2 in. deep. "f" is an incandescent platinum filament set up in a small side chamber placed on A over a slit S_1 .

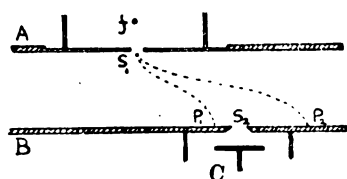
A stream of dry dust-free air is sent through the box. By electric fields of the appropriate sign and strength, ions

* Nolan, Proc. Roy. Irish Acad. xxxv. p. 38 (1920).

of either sign may be dragged from the vicinity of the wire down to S_1 ; those which drift into the air-stream may then be carried across it to the plate B.

Now, if more than one group of ions is present, the paths of these groups will be different. For example, if the ions consist of two groups, one of normal mobility and one of lower mobility, the first will travel along the dotted line striking B at the point P_1 ; the second will travel further down the air-stream and strike B at P_2 (see fig. 1 a).

Fig. 1 a.



If the upper lid of the box is arranged to slide, the points P_1 and P_2 may in turn be made to coincide with the slit S_2 in B. To detect the ions an insulated plate C, electrostatically shielded and connected to an electrometer, is placed under S_2 . A small subsidiary field between B and C ensures that the ions arriving at S_2 are recorded by the electrometer.

Owing to diffusion and self-repulsion the stream of ions increases in width as it travels across the box. It was therefore necessary to obtain the rate of deflexion of the electrometer needle for various positions in the neighbourhood of P, and to deduce the position of S_2 for maximum deflexion graphically. The analysis of spread for different voltages suggested that the effect was mainly due to diffusion, but that self-repulsion became appreciable when the current across the box was large. Diffusion may be cut down by raising the voltage between A and B, thus lessening the time spent by the ions in crossing the box. This, however, lessens the displacement of the ionic stream by the air-current, and cannot therefore be carried beyond a certain limit. Preliminary experiments led us to adopt voltages ranging from 30 to 300 volts across the box and an ionization current sufficiently small to make mutual repulsion negligible.

For maximum resolving power the slits S_1 and S_2 must be very narrow when, however, the number of ions passing through them is too small for measurement. Since the

resolving power was already limited by diffusion, we have remained satisfied with a width of slit of 4 mm. which was adopted early in the work after a few preliminary experiments.

In order to minimize the effect of eddies near the slit S_1 and the loss of ions in passing through it, the slide in its immediate neighbourhood was made thinner than the rest of the box. The lower edges of the slit S_2 were bevelled off for the same reasons.

The movement of S_1 was obtained by making A in two parts. The main fixed part contained a large rectangular opening, over which was placed a brass slide 48 in. $\times$ 7 in. containing the slit at its centre. A good sliding fit between the two parts was ensured by pressure from a number of fairly stout springs. When the air-stream passed through the box, a layer of vaseline around the edges of the slide made any sideways leak of air negligible. Guides were also provided.

The chamber containing the hot filament " f " was made of plastic fire-cement, lined with mica. Copper hooks were inserted in opposite walls for supporting the wire horizontally and parallel to the slit. Platinum wire of S.W.G. 44 was used. The bottom of this chamber was a mica sheet, slotted over the slit S_1 and cemented to the brass slide; the top of the chamber was a thin aluminium sheet. The walls and top were made airtight, because any leak would have caused a flow of air from the main stream through the chamber.

The electrode C under S_2 , together with the electrometer, its key and connexions, were electrically shielded. The sensitivity of the electrometer was usually about 70 to 80 cm. per volt.

During an experiment the following voltages were applied:—(a) " v " between the aluminium top and the filament " f "; (b) " v_1 " between " f " and S_1 ; (c) " V " between A and B; and (d) " v_2 " between S and C.

The Air-stream.—It was of course necessary to use a very steady stream of dry dust-free air. In fig. 1, R is a Keith Blackman rotary blower, rated at 700 revs. per minute, the speed at which it ran most steadily. The air-stream that it furnished to the apparatus was varied by a screw-clip c_1 controlling an alternative escape, and by another clip c_2 in the main flow. T is a steadying chamber of about 2 c. ft. capacity; " r " is a pressure regulator of the type used by Blackwood*; F is an efficient dust-filter.

The speed of the air-stream was measured by reading a

* Blackwood, Phys. Rev. xvi. p. 87 (1920).

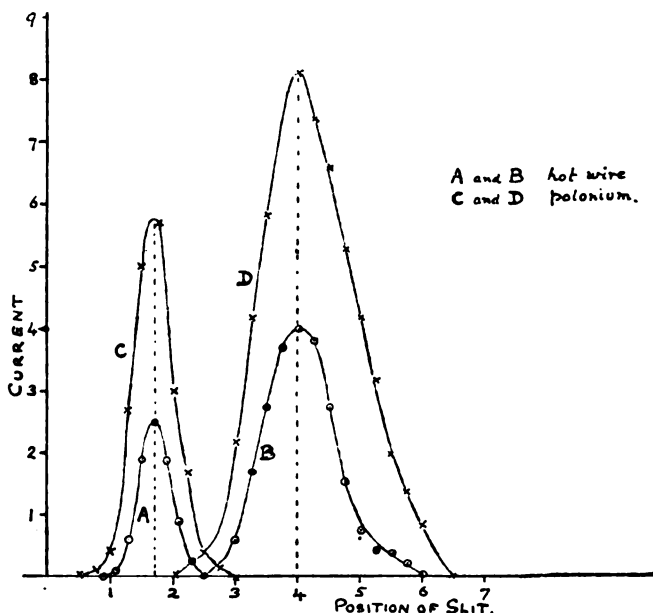
U-tube oil-gauge G placed across the filter, the gauge having previously been calibrated by a gas-meter temporarily inserted in the air-circuit. The readings of flow were usually steady to less than 1 per cent.

D₁ is filled with sulphuric acid and D₂ with calcium chloride. E is a wooden airtight box which tended by its size and shape to produce even distribution and stream-line flow through the mobility box AB.

Experimental Results.

Negative Ions.—Typical results are given in Curves I. The potential differences used in this case were : $v=6$, $v_1=80$, $V=30$, $v_2=6$ volts. The heating current was kept constant

Curves I.



as nearly as possible by means of a microscope focussed on the ammeter needle, and a variable resistance. The air-current varied by less than $\frac{1}{2}$ per cent.

Curve I. A shows the distribution of current at B (due to the hot-wire ions) when no air was flowing, while curve I. B shows the corresponding distribution with the air-current on. It can readily be shown that if " kX " is the velocity of the ions in a field X , " h " the height of the box, and " w " the mean velocity of the stream-line air-flow, then, neglecting

the effect of the sides of the box, which was of considerable width, the displacement of the peak " l " is given by

$$l = \frac{h\nu}{kX}.$$

In other words, when the conditions are kept constant, the displacement is inversely proportional to the mobility of the ions.

The mean value of K deduced from a number of such curves was $K=1.71$. But since the accuracy of the gas-meter was doubtful at the high speeds used in this case, this number can only be regarded as a rough value. In order to ensure that its approximate agreement with the known value for a normal air ion was not accidental, the hot filament was replaced by a sample of polonium arranged to ionize the air in the chamber, but shielded to prevent the direct entry of rays into the air-stream. The result was the curves I. C and I. D, showing in a striking manner the identity of the mobilities of the ions from the two sources.

The increase in the values of the ordinates of the displaced distribution curve is characteristic of all the curves obtained. It seems reasonable to attribute it to slight eddies in the neighbourhood of the slits, carrying through them ions which would otherwise be caught by the sides of the slits.

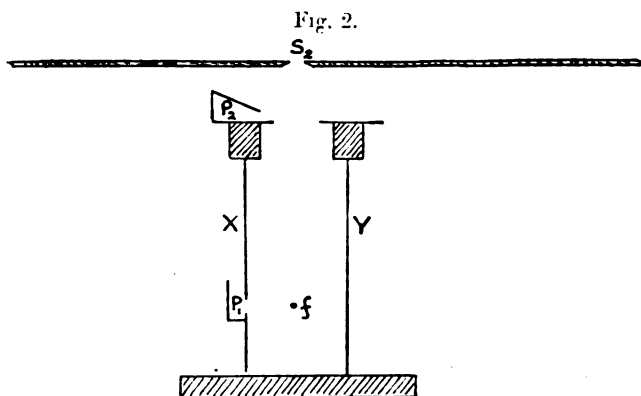
A detailed search was then made for ions of lower mobility, the difference of potential " V " being raised to 144 volts for the purpose. The slide was moved 2.5 mm. at a time to a point at which an electrometer deflexion would have indicated a mobility of 0.005 cm./sec. Throughout the whole time, however, the electrometer was perfectly steady. The age of the ions entering the box was increased by reducing the voltage v from 80 to 30, with, however, the same result. This seems to prove conclusively that *only normal ions were present*.

The apparent discrepancy between this result and that of previous investigators receives, however, a simple explanation. If no larger particles are present, the electrons emitted from the hot filament will attach themselves to molecules and become normal ions. In the absence of an electric field they will be carried upwards by the convection current set up by the hot wire. In our experiments the electric field applied was sufficient to reverse their motion and to pull them out of the hot stream down to the slit. Now, if either ions of low mobility or uncharged particles are emitted from the wire as well, these will also be carried upwards; the

former will be pulled down to the box only by very strong fields, fields too strong to be applied conveniently; the latter will be unaffected by any field. When the normal ions remain with such particles in the same stream, clustering will take place and the mobility of the ions will decrease with time, as McClelland found in his experiments. When the normal ions are rapidly removed downwards from the vicinity of the wire, as in the present work, they will preserve their identity and will alone be observed in the box.

It was felt that some information on the nature of these nuclei might be obtained by inverting the hot filament chamber, placing it under S_2 , and allowing the nuclei as the result of convection to enter the main air-stream through S_2 and to pass across to the electrometer connexion C, now placed above S_1 . Since, in this case, C had to move with the slide, special spring connexions with the electrometer had to be arranged.

The passage of the convection current across from the slit to the top of the box was clearly demonstrated by supplying some ammonium-chloride fumes to the chamber and watching their deflexion down-stream.



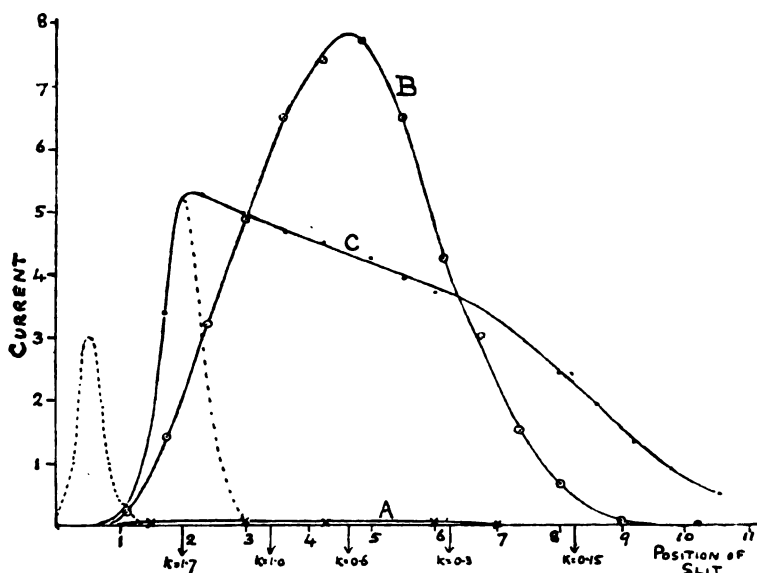
Owing to this convection current, the displacement of the ions by the air-stream was not inversely proportional to their mobility, as in the previous experiments. Some comparative experiments with polonium ions and a convection current from a hot but not incandescent eureka coil gave us an empirical calibration, showing the variation of displacement with mobility for particular values of the air-stream, convection current, and voltage across the box.

Fig. 2 shows the modification of the hot filament chamber which was made. X and Y are parallel plates, 2.8 cm.

apart, between which a potential of 400 volts could be established at will. P_1 is a receptacle in which polonium could be placed so that a horizontal beam of α -rays would ionize the region around the hot filament f . P_2 is an alternative receptacle for introducing ions in the same way into the convection stream after it leaves the space between the plates and before it enters the main box through the slit S_2 .

Three sets of observations were made of the distribution of the ionic stream crossing the box, curves II. showing the results obtained.

Curves II.



Curve II. A.—Filament red hot, with no polonium and no field between X and Y.

Curve II. B.—Filament red hot, with polonium in P_1 and no field.

Curve II. C.—Filament red hot, with polonium in P_2 and field applied. The dotted curves refer to normal ions with and without the air-current.

These curves are fully explained on the view that accompanying the emission of normal ions there is an emission of

uncharged particles in large excess. Thus curve II. A shows only a small current reaching the electrometer, owing to recombination of ions with one another. If, as in case B, a large supply of normal ions is added at the filament, many of the uncharged particles will take up ions which, owing to their consequent decrease in mobility, will recombine far more slowly, and will therefore enter the box in large numbers, as shown in curve II. B. The resolving power of the apparatus does not permit us to say if any particular groups of ions were present, but the smoothness of the curve suggests the existence of a number of ions of all sizes from normal to those of mobility about 0.1, the majority in this particular experiment ranging around a mean value of about 0.6 cm./sec.

It is quite possible that there were also ions of lower mobility; but owing to the eddies which were produced where the convection current struck the top of the box, these escaped detection.

In case C the purpose of the field was to remove all normal ions rapidly from the convection stream. Without any polonium it was then shown that no ions entered the box. Again, the presence of uncharged particles in the convection current was clearly demonstrated by supplying ions to it from P_2 just before it enters the box. Curve II. C shows the result. Clearly in this case an appreciable number of normal ions due to the polonium enter the box, while many others attach themselves to the particles which have probably been coagulating as they rise. The result is a big range of mobility from normal to less than 0.1. A smoothed curve is drawn through the points, because a repetition of the experiment showed that there was no special significance in the local variations. We have recently found that in the detection of uncharged particles from hot wires in dry air we have been anticipated by McClelland and McHenry*. In the last section of a paper on nuclei produced in moist air by ultra-violet light and other sources, they show that uncharged nuclei are driven off from metals by heat in air, whether dry or moist. They showed their presence by passing them over uranium oxide when they combined with normal ions and became large ions, as indicated by the high voltage necessary for a saturation current.

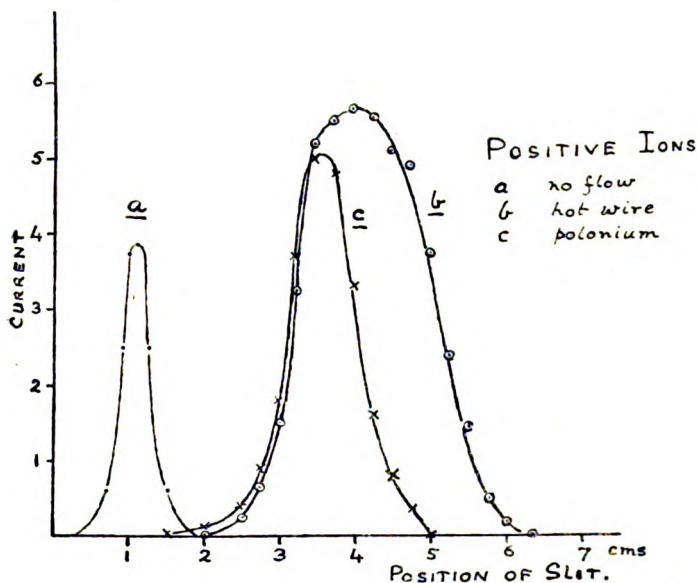
Positive Ions.—Similar experiments were carried out with the positive ions emitted from a hot wire. Typical results are shown in curves III. for positive ions pulled *downwards*

* Proc. Royal Dublin Soc. xvi. p. 282 (1921).

out of the convection stream, the notation being the same as that of curves I. for negative ions.

Comparison with curves I. shows that while the negative ions from polonium and from the hot wire are identical, this is not the case for positives. The wide spread of the positive

Curves III.



ions from the hot wire suggests that they consist of a mixture of ions of various sizes ranging round a mean value of mobility of about 1.0 to 1.1 cm./sec.

Attempts were made to analyse this distribution by repeating with different values of v_1 , but the positive emission from a wire was found to be not steady enough to ensure reliable comparative results.

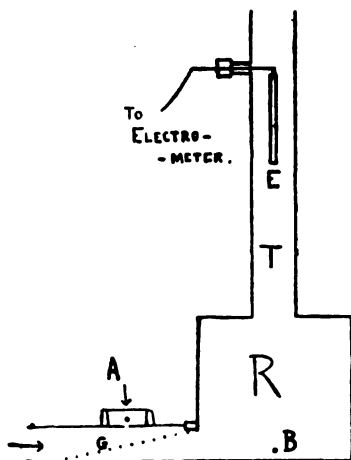
Experiments with the inverted box were also carried out in the same manner as with negative ions with similar conclusions. In fact, the curves obtained are so similar to those in curves II. that it seems unnecessary to reproduce them.

The Second Method.

McClelland's original mobility apparatus was modified to show results which confirmed those obtained above with negative ions. The positive emission was not steady enough

to use it satisfactorily. The arrangement is shown in fig. 3. The source of the ions, either hot wire or polonium, could be placed either in the receptacle A, as in the box method, or in the main stream at B. The electrode E, insulated and connected to the electrometer, was suspended centrally in a long tube T, 7.4 cm. in diameter, the potential of which could be varied. The air-stream, dried and filtered, was driven through a gauze G up the tube T, carrying with it ions from either A or B. The vessel R was inserted to ensure uniform distribution of the ions by turbulence before

Fig. 3.



they entered T. Preliminary experiments with tobacco smoke showed that for the air-speeds used the flow in T near E was stream-line.

Typical results are shown in curves IV., the curves A and B being for the hot wire at A and B respectively. Curve IV.A shows a saturation voltage at about 2.8 volts, which is about the right value for normal negative ions for the dimensions used. Repeating the curve with polonium in A instead of the hot wire gave a curve with the bend at the same point within the limits of experimental error. The absence of any other ions suggested by the apparent horizontal character of curve IV.A beyond the bend was confirmed by taking a series of readings alternating between

700 Prof. A. M. Tyndall and Mr. G. C. Grindley on the

10 and 20 volts to eliminate possible fluctuations in air-speed or accumulator voltages. The table shows that the mean values are the same at both voltages.

Curves IV.

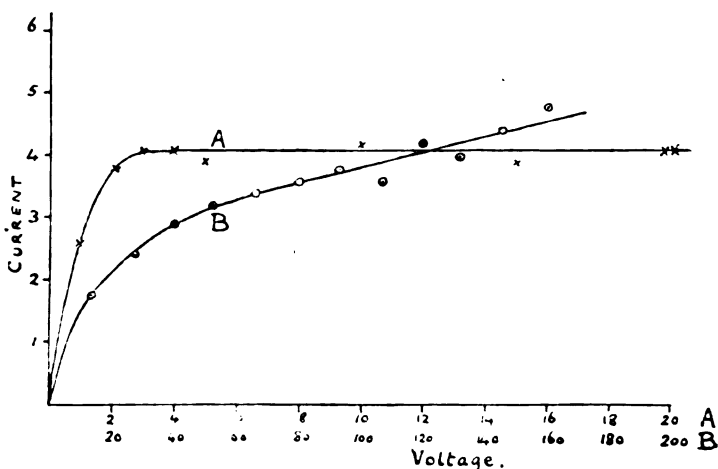


TABLE I.

Electrometer deflexion in cm. per minute.	
10 volts.	20 volts.
8.8	8.7
8.0	8.0
7.6	8.1
8.5	8.3
8.5	8.8
8.8	9.1
9.0	8.8
8.8	8.6
8.50	8.55

Curve IV. B for the wire placed in the air-stream (plotted on a different voltage scale) shows no saturation below 200 volts, which would correspond to a mobility of about 0.005. The general inference to be drawn from the curve, which is convex upwards from an early stage, is that one was dealing with a mixture of mobilities from, say, 0.1 to

less than 0.005. While the curves do not show any evidence of homogeneous groups of ions, it is doubtful whether, if such groups were present, the resolving power was high enough to separate them. These results are in agreement with those of McClelland.

Discussion and Conclusions.

The conclusion to be drawn from the above experiments is that the hot filament emits electrons, positive ions, and a copious supply of uncharged particles. When removed from the vicinity of the particles, the electrons attach themselves to molecules and become normal ions of mobility the same as that of negative ions produced by polonium. In the first method the mobility was measured within $\frac{1}{3}$ of a second from birth and in the second method after 5 to 15 seconds with the same results, showing that, removed from nuclei, the "normal" ion retains its identity unchanged with age.

The positive ions are complex. The approximate coincidence of the left-hand side of the curves III. *b* and *c* strongly suggests that positive ions of mobility about 1.4 in air were given off from the hot wire; but there must also have been many ions present having mobilities from 20 to 60 per cent. lower than this. Hüttermann* has shown that *in vacuo* a hot wire emits not only gaseous positive ions but positive atoms of the metal, and our curve might be accounted for in this way. It is, however, a little doubtful whether a mobility of the order of 1.1 instead of the normal 1.4 could be that of foreign gaseous ions or of platinum atoms in air. Blanc† has carried out some work which suggests that the mobility of the CO_2 ion measured in air is the same as that of an air ion. Similar results have been obtained by Wellisch‡ for ions of methyl iodide in an atmosphere of hydrogen. Again, Franck§ arrives at the same conclusion in the case of the positively-charged recoil atoms of thorium D.

If we accept their results, we must conclude that the positive ions are emitted either as small metallic clusters or as atoms, many of which form clusters by the time they reach the box. The clusters, however, must be small compared with those we usually designate as large ions.

* Hüttermann, *Ann. d. Physik*, lii, 8, p. 816 (1917).

† Blanc, *Journal de Physique*, vii, p. 825 (1908).

‡ Wellisch, *Proc. Roy. Soc. lxxxii*, p. 500 (1909).

§ Franck, *Deutsch. Phys. Gesell. Verh.* xi, 19, p. 397 (1909).

The wire when used for positive emission was only at dull red heat; the convection current from it was therefore less than when it was negative. A certain amount of clustering of ions with uncharged nuclei may possibly, therefore, have taken place before they were separated. The emission of the negative ion as an electron with high mobility, together with the greater convection current, would account for the absence of similar clustered ions in the results for negative discharge*.

The uncharged particles are presumably metallic clusters ranging in size from atoms to metallic dust. Left in association with ions they take up charges and become large ions. No doubt they are responsible for the blackening of filament lamps. Removed from ions they coagulate with time like other particulate clouds.

We are indebted to the Colston Research Society of the University of Bristol for a grant in aid of this research.

Physics Department,
University of Bristol.

LXIV. *The Valency Bond. Electrovalence and Covalence.*
By S. H. C. BRIGGS, D.Sc.†

LANGMUIR (Journ. Amer. Chem. Soc. xli. p. 868, 1919) distinguishes between two types of valency known as electrovalence and covalence. When atoms combine by electrovalence a transfer of one or more electrons takes place from the positive to the negative element, and the resulting ions are then held together by the general electrostatic attraction as in potassium chloride K^+Cl^- . When atoms combine by covalence no electrons are transferred,

* Erikson has recently investigated the positive ions from hot platinum in air. An abstract of his work appears in the *Physical Review* (vol. xxi. p. 720, 1923). He finds that:—"During an interval of the order of 0.30 of a second the initial positive ion changes over into the normal positive ion of mobility 1.36 cm./sec./volt/cm. Since in the initial stage and in the final stage as well, the mobilities are the same as for the positive ion produced in air by the alpha rays from polonium, the conclusion is that the ions are identical. . . . If the platinum is at a very high temperature and the ions are allowed to remain for a short time in the air which has left the platinum surface, they load up and form heavier ions."

It would, however, be premature to discuss the points of difference between his results and ours before a full account of his work appears.

† Communicated by the Author.

but two or more electrons are shared between the atoms in combination, as in methane $\text{H}:\overset{\text{H}}{\underset{\text{H}}{\text{C}}}:\text{H}$, in which each hydrogen atom shares two electrons with the carbon atom.

With certain exceptions which are discussed below, electrovalence compounds correspond to strong electrolytes, and covalence compounds to non-electrolytes. Many previous writers have suggested different constitutions for strong electrolytes and non-electrolytes, but have generally regarded the two types of compound as the extremes of a series with an indefinite number of intermediate stages. Langmuir, however, appears to have gone much further than previous writers in the direction of making a clean cut between the two classes, and has thereby done a considerable service to chemical theory, because the idea of two distinct types has attracted much attention and greatly stimulated chemical thought.

There seems to be an increasing tendency on the part of chemists to accept the view that compounds can thus be divided into two distinct and independent classes, but in my opinion the case for *two clearly defined and separate* types has not been established. The present paper is therefore devoted to some aspects of this problem.

1. *The sharing of electrons.*

Consider a molecule of a strong electrolyte $A'B'$ (an electrovalence compound) formed by the union of an atom of an alkali metal A with the halogen atom B , A giving up its solitary valency electron in order to complete the octet round B , the atom A thereby becoming a positive ion A' , and the atom B a negative ion B' .

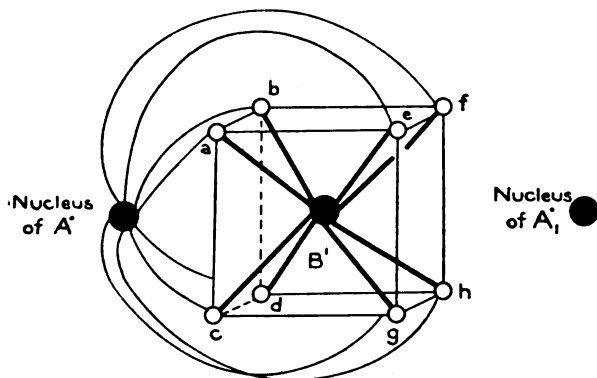
For the sake of simplicity in reasoning, we will adopt the Lewis-Langmuir hypothesis that the eight electrons comprising the completed octet of B' are situated at the corners of a cube, the nucleus of B being at the centre of the cube, and we will make the further assumption that the cube is not distorted in the molecule $A'B'$.

As in previous papers (Trans. Chem. Soc. cxi. p. 253, 1917, cxv. p. 278, 1919; Phil. Mag. xlii. p. 448, 1921), we will adopt the view first put forward by Sir Oliver Lodge ('Nature,' lxx. p. 176, 1904) that the electron and the positive charge when in combination are united by a bundle of a large number of lines of force, so that in a molecule any

given electron or positive charge may be linked up to more than one positive charge or electron respectively.

In the molecule A^+B^- (fig. 1) we may regard the positive ion A^+ as a sphere, because the positive charge is situated at the nucleus, and will therefore act on other ions as if it were distributed equally over the surface of a sphere the radius of which is the nearest distance to which a valency electron in the negative ion can approach the nucleus of A^+ .

Fig. 1.



In this diagram the white circles represent electrons and the black circles indicate nuclei. In order to avoid complication, only the nuclei of the positive ions A^+ and A_1 are shown, all inner shells of electrons being ignored. The negative ion B^- is represented by the cube of valency electrons with the nucleus at the centre, no inner shells of electrons being included. The negative ion B_1^- of the molecule $A^+B_1^-$ is not shown in the diagram.

In the ion B^- we have a kernel with seven positive charges united to eight electrons. Each electron will therefore be linked to the kernel by a bundle of lines of force containing only seven-eighths of the number of lines present in a complete bundle. This will leave one-eighth of a complete bundle to pass from each electron in the octet of B^- to the nucleus of A^+ . The bundles of lines of force are represented diagrammatically in fig. 1 by single lines, the thick lines joining the electrons to the nucleus of B^- and the thin lines connecting the electrons to the nucleus of A^+ .

We see, therefore, that in the electrovalence compound A^+B^- the electrons are shared, but they are shared unequally,

whereas in the true covalence compound they are shared equally. Hence it follows that the difference between electrovalence and covalence is only a difference of degree, the electrons being shared equally in covalence compounds and unequally in electrovalence compounds, the more unequal the sharing the greater the polarity of the compound. If this is the case, it is not possible to divide compounds into two sharply-defined classes, as unequal sharing may include any degree of sharing, from approximate equality to almost complete separation of the ions.

The above reasoning still holds good if the cube is distorted or if the electrons are distributed around B' in some other way and not at the corners of a cube, the effect of such other arrangement being that the electrons will not all be shared in exactly the same manner, but taken altogether will still be unequally shared between A^+ and B' .

2. The crystal structure of strong electrolytes.

Suppose a second molecule $A_1^+B_1^-$ to be brought up against A^+B^- so that the positive ion A_1^+ is between B_1^- and the face $efgh$ of the cube B' . The lines of force from the electrons $e, f, g,$ and h will now have a tendency to attach themselves to the nucleus of A_1^+ , since this nucleus is nearer to them than is the nucleus of A^+ . If a number of molecules were thus joined up in a straight line, we should obtain a chain polymeride in which each ion, positive or negative, would be symmetrically placed with regard to the two adjacent negative or positive ions respectively, and although the original individual molecules would still be present, it would not be possible to distinguish them.

Granted further a suitable relation between the linear dimensions of A^+ and B' , it should also be possible to group the molecules in such a way that an ion A^+ would be adjacent to each of the six faces of the cube B' , and similarly each ion A^+ would be surrounded by six cubes of B' . We should thus obtain the simple cubic space lattice in which sodium chloride and most of the alkali halides crystallize.

If we assume as above that the eight electrons around B' are situated at the corners of a cube, then in the simple cubic space lattice each electron of the octet of B' will be symmetrically placed with reference to the three separate ions of A^+ adjacent to the three cube faces which meet at the corner occupied by that electron. Instead, therefore, of one small

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bundle of lines of force passing from each electron of B' as in the figure of the simple molecule, the small bundle will now be divided into three parts, each portion going to a different positive ion. The valency bond connecting the ions will now be very diffusely distributed, and it is easy to see why the solid acts as a conductor, because, whereas seven-eighths of the lines of force proceeding from each electron in the octet of B' pass to the nucleus of B' , the remainder are divided up between the nuclei of at least three positive ions. Consequently, when the appropriate electrical conditions are applied, B' retains all the valency electrons and the crystal conducts as if it were built up of the ions A^+ and B' .

The crystal structure of a strong electrolyte is often described as a space lattice of positive and negative ions; and this statement is true, in virtue of the electrical conductivity of the crystal. Again, we may also imagine that when a body like potassium chloride crystallizes from aqueous solution, the crystal grows by accretion of individual ions.

As a corollary to the statement that the crystal consists of a space lattice of positive and negative ions, the further conclusion has been drawn that the crystal of a strong electrolyte does not contain molecules. This is clearly a false deduction, because we have seen above that we can derive the crystal structure by a process of *polymerization* of individual molecules, and this is in keeping with experience. As Caven ('Nature,' cviii. p. 210, 1921) has remarked, sodium chloride exists in the form of molecules at *circa* 2000°C . When such a vapour of sodium chloride cools down and solidifies, it can scarcely be expected that each molecule will break up into individual ions before crystallization. The molecules will rather combine with each other, and thus form the crystal of the solid by polymerization as shown above. It therefore follows that the crystal of a strong electrolyte consists of one huge polymerized molecule, the size of which is only limited by the size of the crystal itself.

And although the crystal may be regarded in this way as being built of polymerized molecules, it may equally well be regarded as a space lattice of positive and negative ions. Both points of view are correct, and are mutually complementary, not exclusive.

N.B.—Attention may be drawn to the following analogies,

which may serve to illustrate the point of view indicated in this section :—

- (1) If a number of couples waltzing in a ball-room were to join hands in a ring so that each gentleman had his partner on his right and another lady on his left, a stranger coming into the room would not be able to sort out the original couples, although they would still be there. In a crystal of sodium chloride formed by condensation of the vapour, the original individual molecules are still present but cannot be identified, although the ions can be distinguished just as the individual dancers could be distinguished in the ring.
- (2) A diamond crystal is usually regarded as being built up by the polymerization of carbon atoms. If a more refined method of crystal analysis could be devised which would reveal the actual positions of the electrons just as X-ray analysis discloses the positions of the atoms, such a refined method would indicate that the diamond was built up of electrons and nuclei rather than of atoms.

3. *Compounds intermediate between strong electrolytes and non-electrolytes.*

The properties of aluminium chloride as recently investigated by Biltz and Voigt (*Zeitsch. anorg. und allgem. Chemie*, cxxvi. p. 39, 1923) are of considerable interest for the present discussion. In the solid state aluminium chloride is a conductor, although with the low conductivity of $c. 0.3 \times 10^{-6}$ reciprocal ohms at a few degrees below the melting-point as compared with 3×10^{-6} for silver nitrate. Just at the melting-point the conductivity of aluminium chloride vanishes, so that according to Biltz and Voigt solid aluminium chloride consists of a space lattice of ions, whereas the melted salt contains molecules. We may equally well suppose that the solid is built up of polymerized molecules, the valency forces being diffusely distributed as a result of the polymerization so that the solid is a conductor because the electrons are unequally shared, whereas in the liquid either single or double molecules are present in which the electrons are equally shared between the chlorine and the aluminium, and the liquid is therefore a non-conductor.

2 Z 2

Intermediate between the strong electrolytes and the purely non-polar compounds we have the great majority of the complex salts, most of which have some tendency to dissociation of the complex in solution. Taking the platinichlorides as an example, according to Langmuir we may regard these as electrovalence compounds, the chloride ion being held to the platinum ion by the general electrostatic attraction, or alternatively as covalence compounds in which the platinum atom is surrounded by a disextet of electrons, two of which are shared by the platinum with each chlorine atom. If each pair of electrons is to be saturated they cannot be shared equally, because for this purpose the platinum ion would require six positive charges, whereas it only actually possesses four. It is evident that the distinction between electrovalence and covalence becomes very vague when the theory is applied to complex inorganic compounds.

4. *Langmuir's electrovalence formulæ for certain compounds with non-polar properties.*

There are a number of compounds with the general formula AB_x which have the properties of non-polar substances but which Langmuir regards as electrovalence compounds, because when the octets are completed round the B atoms there are either too few or too many electrons to give an octet round A if A shares two electrons with each atom of B .

In a former paper (Phil. Mag. xlii. p. 448, 1921) it was shown that octet formation may be regarded as a co-ordination of electrons, using the word co-ordination in the sense in which it is applied in Werner's theory of complex salts. If we adopt this point of view, there does not appear to be any particular reason why a positively-charged atom should be able to share *only* eight electrons with negatively-charged atoms which have completed octets. On the contrary, in compounds of the formula AB_x we should expect x to be 2, 3, 4, or 6, corresponding to the sharing of 4, 6, 8, or 12 electrons respectively. By adopting such electron co-ordination numbers for the atom A , the various examples of non-polar compounds to which Langmuir has given electrovalence formulæ become covalence compounds, as might be expected from their general physical and chemical properties.

With electron co-ordination number four we have the metal atoms in such organo-metallic compounds as mercury diethyl and zinc diethyl, $C_2H_5:Zn:C_2H_5$. Such a formula explains the poor conductivity of zinc diethyl compared with the good conductivity of the salt-like sodium ethyl (Hein, *Zeitsch. Electrochem.* xxviii. p. 469, 1922).

The boron atom in boron triethyl provides an example of the electron co-ordination number six. Although boron triethyl is a non-conducting liquid with a low boiling-point, Langmuir gives it an electrovalence formula and explains the peculiarly non-polar properties by suggesting that the field is wholly internal. The best way to ensure such an internal field would be to share two electrons equally between the boron atom and a carbon atom of each of the three groups, as this could be done without setting up strains in the non-polar ethyl radicles, and a purely non-polar molecule would thus be obtained.

Carbon tetrachloride would be written as a covalence compound, the carbon atom having the electron co-ordination number eight, whereas Langmuir prefers an electrovalence formula to harmonize with the electrovalence formulae given to sulphur hexafluoride etc.

Sulphur hexafluoride is a tasteless and odourless gas, chemically as inert as nitrogen. Langmuir regards it as an electrovalence compound, with the field wholly internal. Sulphuryl fluoride, also a tasteless and odourless gas, is regarded by Langmuir as a covalence compound, because a formula can be given to it by the equation $v = 8n - 2p$,

$$\begin{array}{c} F \\ | \\ O-S-O \\ | \\ F \end{array}$$

the formula being written $O-S-O$. It should be re-

marked, however, that in this formula the sulphur is left with two positive charges and the oxygen atoms have each a free negative charge. This formula suggests properties quite different from those of a tasteless and odourless gas. The difficulty vanishes completely, however, if we give both compounds a covalence formula in which the sulphur atom has an electron co-ordination number twelve, sharing a pair of electrons with each fluorine atom in SF_6 , and two pairs with each of the oxygen atoms as well as one pair with each fluorine atom in SO_2F_2 .

5. *Acids, bases, and salts.*

Lowry ('Chemistry and Industry,' xlii. p. 43, 1923) has recently suggested that hydrogen differs from other positive elements in that it is able to enter into various stages of combination from true covalence to strongly-marked electrovalence, and adopting Langmuir's view, he further states that this is the reason why there are strong and weak acids, strong and weak bases, but no weak salts.

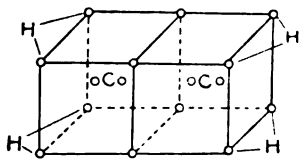
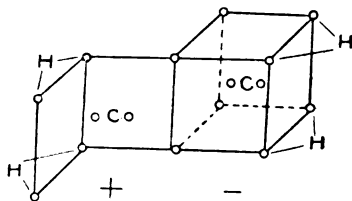
From the chemists' point of view it is difficult to understand the statement that there are no weak salts, because in the series KCl , CdCl_2 , CdI_2 , HgCl_2 , $\text{Hg}(\text{CN})_2$, WF_6 we have a gradual diminution in polar properties from the strong electrolyte KCl to the non-polar gaseous WF_6 . If we accept the view that electrovalence and covalence differ only in degree, the series presents no difficulty, and it is not necessary to introduce special explanations such as Langmuir brings forward, assuming the existence of "strong secondary valence forces" which prevent the electrolytic dissociation of HgCl_2 and $\text{Hg}(\text{CN})_2$.

The reason why hydrogen forms non-electrolytes so much more readily than other positive elements is doubtless due to the fact that the hydrogen ion is a nucleus only, as suggested by Lowry. Other positive ions, in comparison with the hydrogen nucleus, may be regarded as very large spheres with the positive charge distributed over the surface. The conditions for the formation of non-polar compounds by such positive ions are strictly limited, as explained some years ago (Briggs, *Trans. Chem. Soc.* cxv. p. 281, 1919), and this is the reason why most salts are strong electrolytes.

6. *Lowry's mixed double bonds.*

In a recent paper (*Trans. Chem. Soc.* cxxiii. p. 822, 1923) Lowry has suggested that the double bond in organic compounds usually acts as if it contained one covalence and one electrovalence, and has shown that this theory can be successfully applied to many branches of organic chemistry. The formula for ethylene $\text{CH}_2=\text{CH}_2$ obtained in this manner raises a question of some interest. Polar compounds generally have a tendency to polymerize, and a substance of the formula $\text{CH}_2^+-\text{CH}_2^-$ might be expected to be a solid at the ordinary temperature rather than a monomolecular gas.

The difficulty can be avoided if Lowry's formula represents an active phase through which every molecule passes, but in which only a small proportion of the molecules exist at any given instant*. Such an active phase might arise by the distortion of the molecule due to thermal agitation or some other cause, two of the shared electrons in Langmuir's formula being taken away from one carbon atom as to leave only a single valency bond. This is shown diagrammatically in fig. 2 *a*, which represents the normal molecule as pictured by Langmuir, and fig. 2 *b*, the distorted molecule corresponding to the formula $\text{CH}_2^+ - \text{CH}_2^-$. The

Fig. 2 *a*.Fig. 2 *b*.

distorted molecule might be expected to swing back at once to the symmetrical form *a*; and it is not necessary to assume that the two internal electrons of the positive carbon atom come out to the surface in order to complete the octet. Similar considerations would apply to benzene, which is a truly non-polar compound according to Sir Joseph Thomson (Phil. Mag. xxvii. p. 764, 1914).

If this view of Lowry's ethylene formula is accepted, it is clear that the difference between electrovalence and covalence is only a question of degree, due to the varying positions of the electrons.

7. The magnetic theory of valency.

In the preceding sections it has been assumed throughout that the valency forces are purely electrical. It was shown in section 1 that electrons are shared in electrovalence compounds (strong electrolytes), but that they are shared unequally. Since electrons are shared equally in true covalence compounds such as a molecule of oxygen in which both atoms are electrically neutral, it was suggested

* In a more recent paper Lowry has expressed a similar view. (Trans. Chem. Soc. cxxiii. p. 1866.)

that covalence corresponds to equal sharing of electrons and electrovalence to unequal sharing, the difference between electrovalence and covalence being therefore only a difference of degree.

The actual relation between electrovalence and covalence, as these terms are used by Langmuir, does not appear, however, to be quite as simple as this, since Langmuir has given covalence formulæ to the complex ions in co-ordination compounds in which the electrons cannot be shared equally, as shown in section 3 above.

Again, electrovalence compounds are usually regarded as strongly polar, and covalence compounds as non-polar; but instances were given in section 4 in which Langmuir has suggested electrovalence formulæ for non-polar compounds. It was shown, however, that it is possible to give these compounds covalence formulæ by adopting the principle of the co-ordination of electrons.

If the views of Oxley (*Proc. Roy. Soc. A*, xcvi. p. 264, 1921) and Peirce (*Phil. Mag.* xlv. p. 317, 1923) and others are accepted, in electrovalence compounds the valency forces are electrostatic, and in covalence compounds the valency is due to magnetic attraction between two electrons, the doublet occurring where electrons are "held in common" in Langmuir's theory of chemical combination. From this point of view there would be an actual difference of kind between electrovalence and covalence. It would then be necessary to explain the gradation in properties from strong electrolytes to non-electrolytes familiar to the chemist.

Do these different degrees of polarity represent different degrees of electrovalence? and, if so, is it possible to have non-polar electrovalence compounds with equal electrostatic sharing of electrons as well as non-polar covalence compounds due to magnetic attraction?

If there are two such types of non-polar compounds, by what tests can they be distinguished? If there are not two distinct types of non-polar compounds, what is the physical interpretation of the properties of weak electrolytes intermediate between strong electrolytes held together by electrostatic forces and non-electrolytes due to magnetic attraction?

The words electrovalence and covalence are coming into general use in chemical literature, and it is highly desirable from the chemist's point of view that a precise physical definition should be given to these terms.

Addendum.

The substance of this paper was given in the form of an address to the Priestley Club, Leeds, on March 13th, 1923. The paper was sent in for publication in June 1923, before the discussion on valency at Cambridge, arranged by the Faraday Society.

In a paper published in 1923, Knorr (*Zeitschrift für anorganische und allgemeine Chemie*, cxxix. p. 109) showed that if Bohr's theory is accepted and it is assumed that atoms combine by the sharing of electron orbits rather than by the sharing of electrons, then there is no clear distinction between electrovalence and covalence ("Ionenbindung und Atombindung") (see also Fajans, *Naturwissenschaften*, xi. p. 165, 1923). In this connexion it should be observed that "the sharing of electron orbits" and "the co-ordination of electron orbits" may be substituted in the above paper for the "sharing of electrons" and "the co-ordination of electrons" without affecting the general argument.

LXV. *An Apparatus for Purification of Radium Emanation.*
By VICTOR F. HESS, Ph.D.*

RADIUM salts are so precious that handling of radium preparations in small, thin-walled glass tubes always involves a certain risk. Since radium itself does not emit any gamma rays of high penetrating power, while the emanation with its successive products gives off alpha, beta, and gamma rays, it is in most cases preferable to use "emanation tubes"—i. e. small glass tubes containing emanation instead of radium. The walls of these emanation tubes can be made thin enough to allow the passage of alpha rays †.

Sir William Ramsay and F. Soddy ‡, Sir Ernest Rutherford §, A. Debierne ||, S. C. Lind ¶, William Duane **, and others have described apparatus by means of

* Communicated by the Author.

† E. Rutherford and T. Royds, *Phil. Mag.* (6) xvii. p. 281 (1909).

‡ W. Ramsay and F. Soddy, *Proc. Roy. Soc. A*, lxxiii. p. 346 (1904).

§ E. Rutherford, *Sitz. Ber. Wien. Akad. d. Wiss.* vol. 117. p. 925 (1908); & *Phil. Mag.* (6) xvi. p. 300 (1908).

|| A. Debierne, *Compt. Rend.* vol. 148. p. 1264 (1909).

¶ S. C. Lind, *Sitz. Ber. Wien. Akad. d. Wiss.* vol. 120. p. 1709 (1911). Also R. E. Nyswander, S. C. Lind, and R. B. Moore, *Astrophys. Journ.* liv. p. 292 (1921).

** W. Duane, *Physical Review*, (2) v. p. 311 (1915); *Boston Med. and Surg. Journ.* vol. 177. p. 787 (1917).

which it is possible to pump off practically all emanation produced in a given radium solution every day and to remove the gaseous impurities. The purified emanation finally is sealed up in little glass tubes very much smaller than the tubes which contain the equivalent amount of radium in form of highly concentrated salts. All these devices or "emanation apparatus," as they are called commonly, have the advantage that the precious radium solution is permanently kept in a vault, safe from any damage, fire, or theft.

These emanation apparatus are particularly advantageous for hospitals and similar institutions where radium work is done every day. Within the limits of the amount of radium at disposal, the operator can produce tubes of almost any desired strength by subdividing the capillary glass tube in which the purified emanation finally is sealed. One gram of radium in solution gives a daily output of about 160 millicuries of emanation. Pumping off every day, the operator produces out of 1000 mg. of radium about 1020 millicuries per week. In the following week, the tubes of the first week are still strong enough, so that the laboratory or hospital after a short time has a great number of emanation tubes of various strengths at disposal.

In aqueous radium solutions together with emanation a number of other gases are formed continuously by the action of the radiations: large quantities of hydrogen, oxygen, carbon dioxide, chlorine or bromine, and traces of organic vapours which are generated by the action of emanation on stopcock grease. In addition, a very small amount of helium is produced by the radioactive decay.

The apparatus for purification or concentration of emanation are working on the principle of certain chemical reactions and physical effects such as :—

- (a) Combination of H and O by sparking or by exposure to an incandescent filament.
- (b) Absorption of water-vapour by P_2O_5 or other chemicals.
- (c) Removal of excessive amounts of hydrogen by oxidation with a heated copper-oxide coil (W. Duane), or
- (d) Separation of emanation by imbedding the end of the capillary tube in liquid air (liquefaction of emanation).

The principles (a), (b), and (c) are used in Duane's apparatus (*l. c.*) and in a similar improved apparatus of G. Failla* (Memorial Hospital, New York City), who

* 'Archives of Radiology and Electrotherapy' (June 1910).

designed special vacuum stopcocks with graphite instead of vacuum grease.

For continuous use all these apparatus involve certain difficulties. They require skillful, well-trained operators. Whenever a break occurs in an elaborate apparatus, it can be repaired, as a rule, only by a professional glass-blower. Sometimes repairs are impossible, because the glass by the action of the rays becomes brittle and does not seal with fresh glass of the same sort. In order to avoid delays in case of breakage, G. Failla has adopted the principle of using a "twin apparatus" consisting of two identical glass apparatus connected to the same radium solution.

The apparatus which give a high-grade purification, such as Duane's and Failla's, cannot be used efficiently with much less than 500 mg. of radium in solution.

The author intended to construct an apparatus for purification of radium emanation simpler and smaller than these elaborate machines primarily for the use of physical and chemical institutes, for small hospitals, and for the average radium practitioner who cannot afford to buy 500 or 1000 mg. of radium.

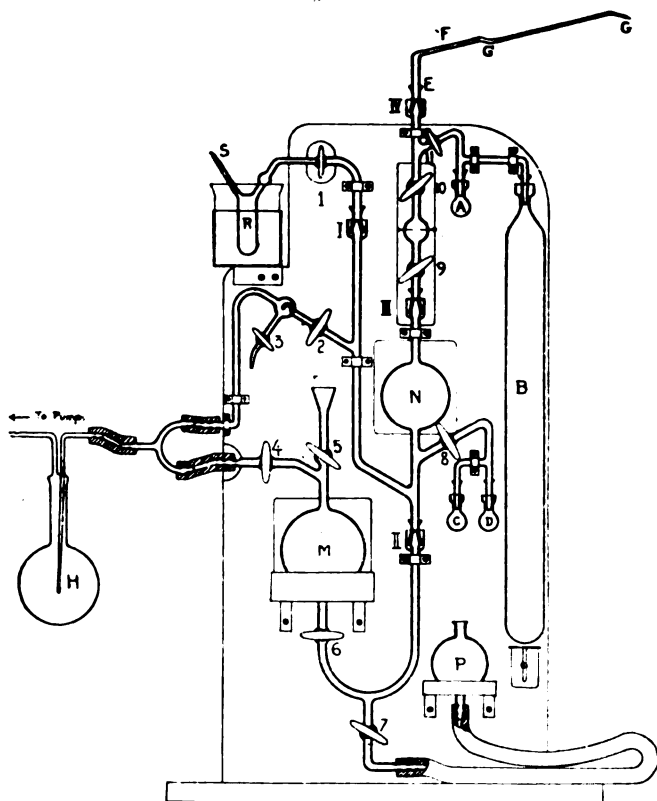
Fig. 1 shows the new apparatus in a vertical section. The heavy lines mark the glass apparatus, which is mounted on a wooden board 70 cm. high and 36 cm. wide. The whole apparatus, together with the radium solution (R), can be kept in a safe cabinet of the usual size. The apparatus is made in five parts, which can be detached and re-assembled within half-an-hour. In fig. 1 the joints (mercury-sealed) are marked with I, II, III, and IV. Cleaning of the apparatus by mechanical means (iron wire with cotton wound around) or liquids is therefore very easy. This is important, since all glass apparatus in which mercury comes in contact with emanation are gradually covered with layers of mercury compounds (chloride or bromide). Internal cleaning of Duane's or Failla's apparatus is not possible without cutting glass connexions and resealing, which sometimes causes serious difficulties, as mentioned above.

The new apparatus is constructed in such a way that every joint can be replaced by an exactly fitting spare joint. The radium solution itself is detachable, and its glass joint I (fig. 1) can be made to fit a second apparatus ("twin principle"). It is also possible to use several bulbs with radium solutions in connexion with one apparatus.

The evacuation can be performed by any rotary pump giving a vacuum of at least 0.01 mm. mercury. The

"Cenco-Hyvac" rotary pump (produced by the Central Scientific Co., Chicago), giving a primary vacuum of about 0.001 mm., was found very suitable. An additional device (shown in fig 1 (B) and discussed later) makes it possible to obtain in the apparatus a hundredfold better vacuum without using an additional pump.

Fig 1.



The apparatus is made of soft glass. The inside part of every stopcock is made of "pyrex" glass. It was found that sticking of these stopcocks never occurred even when very little grease is used.

In general, the use of ground-joints and greased stopcocks was not avoided, as it was found that the volume of foreign gases was not increased perceptibly by the use of grease in these connexions. This seems to be contrary to the

experience of other observers. But in fact the emanation really is in contact but a very short time (about ten minutes) with most of the greased stopcocks and joints (like Nos. 9, 10, III and IV in fig. 1). Therefore the amount of organic vapours liberated by the action of the emanation is practically negligible.

Only one stopcock is in permanent contact with emanation—No. 1 in the figure. If very high purity of emanation is desired, it is well to grease this stopcock with orthophosphoric acid very carefully once a week. The other communications have to be greased with good vacuum grease once a month when used daily. The radium solution (chloride or bromide in distilled water with barium chloride and a few drops of hydrobromic or hydrochloric acid) is filled into R (fig. 1) through S, and this tube immediately afterwards sealed. If not more than 200 mg. of radium are used, the volume of R can be less than 30 c.c. The solution is surrounded by a beaker and a brass cylinder (mounted on the board) for protection.

The apparatus is connected to the vacuum pump by means of the cocks Nos. 2 and 4 (see fig. 1) and two pieces of vacuum rubber hose with a U-shaped tube. H is a trap-flask. Stopcock No. 4 is used to suck the mercury back to its normal level above joint II.

The mercury bulb N has a volume of 360 c.c., while M contains 500 c.c. The small side bulbs A and C contain some pure P_2O_5 ; bulb D some KOH to absorb moisture and carbon dioxide.

Between the stopcocks Nos. 9 and 10 is the explosion chamber. Two platinum wires, leading to a small induction coil fed by two dry cells (3 volts), form a gap of 6 mm. The character of the discharge gives a very good idea about the vacuum reached, and therefore it was found needless to use a McLeod manometer in addition.

The apparatus is filled with mercury in M and the neighbouring tube to just above the joint II. The levelling bulb P and the vacuum hose attached to cock No. 7 must be filled with mercury. Air bubbles have to be driven out carefully.

The apparatus is so tight that within 24 hours no change in the character of the discharge in the explosion chamber (X-ray vacuum, green fluorescence of the glass walls) can be detected.

Before the experiment one or two little pieces of copper oxide in wire form (5 mm. long) are introduced in the end capillary tube at G and G' (fig. 1), and one of them shaken.

down to the end which is slightly bent down. Inside the end-tube in E a granule of molten phosphorus pentoxide is placed for the final purification of the emanation.

The radium solution, immediately after filling, contains some occluded air which has to be removed. This is done by evacuating the whole apparatus: as soon as stopcock No. 1 is turned on, the solution begins to boil. It is necessary to control this boiling by closing the stopcock partly as soon as bubbles begin to spurt up too fast. When the solution has boiled twice for about 30 seconds and the apparatus has been again evacuated till good Röntgen vacuum is reached (indicated by green fluorescence in the explosion chamber) everything is ready for the first experiment.

After a suitable period of accumulation of emanation—for instance, on the next day—the vacuum is tested first and if found satisfactory the air-sack B (fig. 1) is used in the following way to improve the vacuum:—Stopcocks No. 8 and 4 are closed and Nos. 5 and 6 are turned on slowly. The mercury is driven up in N by the atmospheric pressure, and stopped as soon as it reaches the branch immediately below stopcock No. 11. Then this stopcock is closed. Most of the air residues which were in N and the vertical tube are now caught in the large tube B. Then the mercury is sucked back by the rotary pump after closing stopcock No. 5 and opening No. 4. Now the pressure is so low that no visible discharge can pass the spark-gap. Taking into account the ratio of the volume of the capillary tube EFG to the volume of the air-sack B, we find that a vacuum of about 0.00001 mm. mercury is reached.

Now stopcock No. 10 is closed, and No. 1 turned on very slowly until the radium solution begins to boil; 30–50 seconds' boiling is sufficient. Most of the emanation is now in the explosion chamber and in N. After closing stopcock No. 1, the emanation is pushed up from N into the explosion chamber by admitting air into M through stopcock No. 5. As soon as the mercury has filled N and touches the lower part of the stopcock No. 9 this cock and No. 5 are closed, and the mercury sucked back by the rotary pump till the normal level above joint No. II is reached. Now the solution is boiled a second time by opening stopcock No. 1 for another 30 seconds. By this procedure the last traces of emanation are drawn into the bulb N. After closing No. 1 again, these traces of emanation, together with the foreign gases, are pushed up into the explosion chamber until this is filled with mercury to its lower third.

The gases mixed with emanation contain much hydrogen and oxygen. A single spark of the induction coil between the electrodes causes a bright flash and combination of hydrogen with the equivalent amount of oxygen to water, which is largely deposited on the walls of the explosion chamber.

Now stopcock No. 10 is opened (No. 11 remains closed), and by slowly turning cock No. 6 the mercury rises above the stopcock No. 10, leaving the water behind in the explosion chamber. As soon as the mercury reaches the joint No. IV, its further movement is stopped by shutting off cock No. 6. Now we have the emanation mixed with the excess of hydrogen, CO_2 , water-vapour, helium, and traces of organic vapours. Hydrogen is removed by heating the tiny copper-oxide wires at G and G' subsequently from outside by a very small pointed gas flame. It is sufficient to heat these copper-oxide wires to dull red heat for about 2 minutes, in order to reduce the hydrogen. The water-vapour is absorbed by the granule of P_2O_5 within the tube near E. Carbon dioxide can be removed by using a small granule of KOH within the end-tube at E in addition. But ordinarily this was found unnecessary. After heating, the gases are allowed to be in contact with the chemicals for 5 minutes. Immediately after, the stopcock No. 6 is opened, and the mercury climbs up towards the end of the capillary tube G. In order to have the emanation tube free from copper oxide, the pointed flame is applied at the very end of the tube until the glass collapses, and is drawn off together with the copper-oxide wire sealed within.

When working with 100 mgs. of radium in solution every day, the residual gases have a volume of about 30 cubic millimetres with 15 millicuries of emanation within, at a pressure of one-fifth of an atmosphere.

Before sealing we can obtain further reduction of the volume by the use of the levelling bulb P (fig. 1), closing cock No. 6 and opening No. 7. It is not advisable, however, to lift P above cock No. 10, because in sealing off the end-tube the pressure inside is naturally increased, and a perforation of the heated thin-walled tube is possible.

The final concentration in the end-tube is about one millicurie of emanation per cubic millimetre. This is sufficient for most purposes.

Sealing off the end-tube is very easy: the tube is held with a forceps, and drawn off as soon as it collapses at the point where the flame is applied immediately above the level of the mercury.

The makers of the apparatus provide 20-40 end-tubes

720 *Apparatus for Purification of Radium Emanation.*

(like EFGG') fitting to the same joint (No. IV in the figure), so that the apparatus can be operated about one year before any replacement of capillary tubes is necessary. New capillary end-tubes can be drawn out by any glass blower from the bent end E (see fig. 1). Thus the 20 or 40 upper tubes EFG can be used for many years.

In case the purification process as described above is not sufficient for special experiments (for instance, spectral analysis), the liquid-air method can be applied in addition to the method described above, using the same apparatus.

In this case the capillary end of the tube is bent down vertically, and immersed in a small Dewar beaker containing liquid air. The mercury in EF is drawn back to E. A vertical side-tube, provided with a stopcock just above E, enables one to pump off all residual gases while the emanation in the end capillary tube is in the liquid state. Then the stopcock above E is closed, the liquid air removed, and the mercury pushed up towards the very end. This method gives the highest purification.

Ordinarily the concentration of 1 millicurie per cubic millimetre in the end-tube will suffice for physical, chemical, and medical application of radium emanation.

Experiments with this apparatus were continued over a period of one year. The actual amount of emanation in the small capillary tubes was in the average 93 per cent. of the total amount accumulated in the solution in a known period.

The apparatus is made by the U. S. Radium Corporation, New York and Orange, N. J., U. S. A.

I am much obliged to Dr. Edwin D. Leman, Chief Chemist of this firm, for many suggestions and valuable assistance in the course of the experiments.

Summary.

An apparatus is described which gives quick and efficient purification of radium emanation from foreign gases such as hydrogen, oxygen, carbon dioxide, etc., which are mixed with it in radium solutions. The process is based on a combination of known chemical reactions: the equivalent amounts of hydrogen and oxygen are recombined by the electric spark; water-vapour and carbon dioxide are absorbed.

The final purification is done by heating a small piece of

copper-oxide wire in the capillary tube from outside, thus reducing the excess of hydrogen.

The apparatus is small enough to be kept in a safe together with the radium solution attached to it. Only one automatic vacuum pump is used. A special device enables one to increase the vacuum given by the pump about a hundred times. The apparatus is detachable, and can be cleaned inside without cutting any glass connexions. The process of purification of emanation takes about 15 minutes, and gives a final concentration of approximately one millicurie per cubic millimetre. Whenever higher concentration is required, liquid air has to be used in addition. The apparatus can be used with solutions containing from 50 milligrams of radium upwards.

LXVI. *The Distribution of Colloidal Particles.*

By E. F. BURTON, B.A., Ph.D., and J. E. CURRIE, M.A.*

THE problem of the distribution of colloidal particles was first brought into prominence by the work of Perrin†, which showed that for regions very near the surface of a given volume of solution the law of distribution of the particles is analogous to that regulating the distribution of molecules of gas in the atmosphere. Although the original experiments were carried out for distances up to only one-tenth of a millimetre, the impression that it holds for all distances has got abroad‡.

Theoretical considerations§ show that the law cannot hold for distances even of the order of a few centimetres. Actual experiments by Porter and Hedges|| and by one of us§ have shown that the distribution is uniform to within an exceedingly short distance from the surface of the solution.

In the paper referred to above§ one type of the experiments described consisted in letting a sample of colloidal solution stand in a vertical tube for some two months, after which the concentrations at different layers were measured. In private correspondence with various workers, criticism of this experiment was offered on account of the fact that

* Communicated by the Authors.

† Perrin, 'Atoms,' tr. by Hammick (Constable) (1916).

‡ See Svedberg, 'Colloid Chemistry' (Chem. Cat. Co., 1924), pp. 96-102.

§ Burton & Bishop, Proc. Roy. Soc. A, vol. c. p. 414 (1922).

|| Porter & Hedges, Trans. Faraday Soc. vol. xviii. pt. 1, Oct. 1922.

rigid precautions were not taken to protect the tubes during the two months from changes of temperature and from light.

Apparatus.

In the following paper the record is given of similar experiments in which more elaborate care as to the protection of the tubes was taken. Four tubes (as illustrated in fig. 1)

Fig. 1.

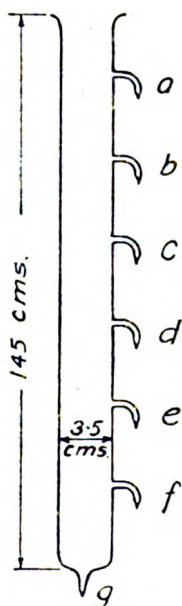
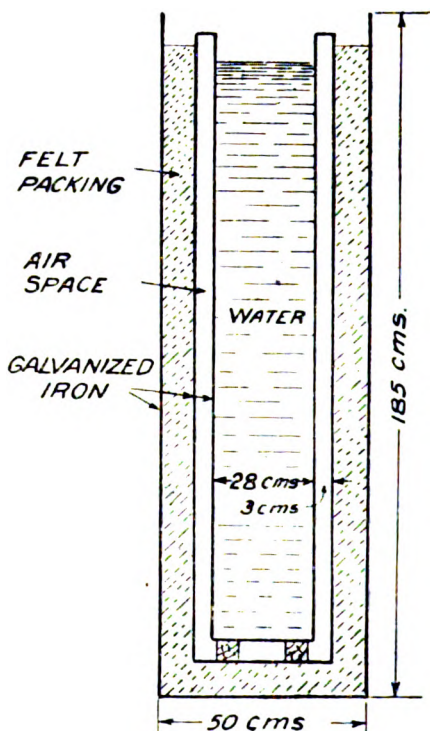


Fig. 2.



were filled respectively with samples of the following solutions: gamboge, arsenious sulphide, copper (Bredig), and silver (Bredig). All of the tubes were suspended so as to be immersed almost to the top in water contained in a large thermostat which was protected from external temperature changes by an air-gap and a space filled with felt (fig. 2). The thermostat was provided with a stirring paddle which

was used from time to time. The tubes were left in this water-bath for a period of four months, during which time there were no abrupt changes in temperature of the water; during the period the temperature of the room gradually changed, due to the starting of the heating system in the building, through about 7°C. , and caused a slow change in the temperature of the water of that amount. However, there were no abrupt changes in temperature which would give rise to convection currents. The tubes were kept in darkness up to the time samples were tested.

The samples were drawn off by breaking the points *a, b, c, d, e, f, g* as the tube was raised from the water. In every case the small amount of sediment in the ends of *a, b, c*, etc. was allowed to run off before the sample was taken.

Experimental Results.

In the use of each of the above colloidal solutions each of the seven samples was treated as follows:—

- a.* Two independent determinations of the concentrations were made.
- b.* Tests were made of the electrical conductivity of the sample, the electrical mobility of the particles, and counts were made of the number of particles per c.c.

With regard to those tests made under (*b*), it would be a waste of space to record all the individual determinations of the various quantities; but with each of the solutions, there was no indication of any change in any of these measured quantities for samples taken from various heights.

In Table I. there are recorded the results of the determinations of concentrations.

TABLE I.

No. of Layer.	Average distance from top.	Gamboge (mgms. per 50 c.c.).	Arsenious Sulphide (mgms. per 50 c.c.).	Copper (mgms. per 50 c.c.).	Silver (mgms. per 50 c.c.).
I.....	8.5 cms.	25.7	106.4	3.9	3.3
II.....	27.5 "	26.7	109.5	4.3	3.9
III.....	48.5 "	26.8	104.9	4.3	3.1
IV.....	69.5 "	26.5	105.4	4.2	3.6
V.....	90.5 "	27.2	108.0	4.4	3.5
VI.....	111.5 "	26.0	106.9	4.3	3.5
VII.....	132.5 "	25.6	105.5	4.4	3.3

From these results there seems to be little room for doubt that the particles in these solutions are uniformly distributed and that this distribution is regulated by some mutual action of the particles. In spite of what has been written to the contrary, the possession of like electrical charges seems to offer the most straightforward explanation. It is usually assumed that the existence of the so-called Helmholtz layer leaves the combination, particle plus Helmholtz layers, as an electrically neutral entity. However, the rational view of the Helmholtz double layer, in view of the accepted theory of electrolytic dissociation, is that close up to the particle (or on its surface) is a layer of ions of one sign, while scattered about in a volume outside the particle is an atmosphere of liquid containing ions of both signs, but with those of sign opposite to the charge on the particle in greater concentration than those of the other sign. This might result in the particle having an effective charge of one sign which might easily be the source of mutual repulsion between the particles.

LXVII. *On a Diffusion Theory of Comets.* By HEINRICH MACHE, Ph.D., *Professor of Physics at the Technical High School, Vienna* *.

IF we introduce a bead of easily fusible glass (O) a few millimetres above the tip of the inner cone (K) of the flame of a Bunsen burner, a sharply-defined yellow space (ss') of luminous sodium vapour is formed in the current of gas which is ascending vertically with large velocity at that point. This space envelops the bead, and broadens out in the higher parts of the flame, as seen in fig. 1. Provided the gas-pressure is not too large, it can readily be calculated that the "critical velocity" (Reynolds) will not be exceeded even in these parts of the flame, so that the flow remains laminar, and the sodium vapour developed from the bead is driven into the hot gas solely under the influence of diffusion. The fact that the vapour extends beneath the bead in the direction OA is proof of the high values of the coefficient of diffusion assumed at high temperatures, and at this point diffusion must be able to more than counter-balance the upward flow.

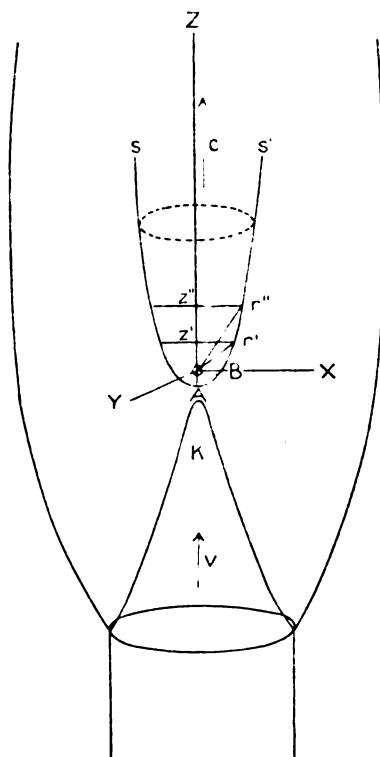
H. A. Wilson † has shown how the coefficient of diffusion

* Communicated by the Author.

† Phil. Mag. xxiv. p. 118 (1912); cf. also Proc. Camb. Phil. Soc. xii. p. 406 (1904).

of sodium vapour in the gas of the flame can be determined from measurements of the luminous figure ascending from the glass bead. In § 1 his theory of the phenomenon will be briefly developed, and extended as far as seems necessary in view of the application in § 2.

Fig. 1.



We shall assume that in the space with which we are concerned the flow of gas is everywhere parallel to the axis. This assumption is valid when we restrict ourselves to the central part of the flame above the cone, and can be tested by mixing particles of carbon with the gas, these becoming luminous in passing the cone of combustion and following the lines of flow of the gas. Our second assumption might appear more open to doubt. We shall assume that the same density of vapour exists everywhere along the boundary of the luminous space. In any case, the boundary is sufficiently sharp to enable us to assume that the density gradient at the

limit of visibility is still very large, particularly when we remember that the brightness increases slowly with the density of the vapour and the thickness of the radiating layer*. The limit of visibility must then also represent a surface of almost uniform vapour density.

§ 1. In the theory of the conduction of heat we find an analogous problem to every problem in diffusion; and for this reason it will be advisable to deal first with the problem in the conduction of heat which is analogous to our present problem.

We suppose a medium flowing with constant velocity c in, say, the direction of the positive z -axis. Furthermore, we shall suppose that a source of heat of invariable intensity is acting permanently at a definite point in the medium, this point being at rest as compared with the medium. For the purpose of simplicity let us consider this point to be situated at the origin of the stationary system of coordinates. In the course of time a stationary state would be established, and we have to calculate the form of the isothermal surfaces for this stationary state. In reality this requires the solution of the differential equation:

$$k^2 \left(\frac{\partial^2 \vartheta}{\partial x^2} + \frac{\partial^2 \vartheta}{\partial y^2} + \frac{\partial^2 \vartheta}{\partial z^2} \right) - c \frac{\partial \vartheta}{\partial z} = 0.$$

Now we can reduce our present problem of heat conduction in the moving body to one in a stationary body, by imagining the permanent source of heat which is actually acting at the origin to be replaced by sources of heat that act instantaneously at every point of the z -axis at different times. Each of these instantaneous sources of heat determines a distribution of temperature in the conducting medium, which is readily calculable for a definite time, and by summation we obtain the solution of our problem.

In a stationary medium we have the equation

$$\frac{\partial \vartheta}{\partial t} = k^2 \left(\frac{\partial^2 \vartheta}{\partial x^2} + \frac{\partial^2 \vartheta}{\partial y^2} + \frac{\partial^2 \vartheta}{\partial z^2} \right),$$

of which the following expression is a solution:

$$\vartheta = \frac{1}{t^{3/2}} \cdot e^{-\frac{x^2+y^2+z^2}{4k^2t}},$$

or, transforming the coordinates, we have

$$\vartheta = \frac{1}{t^{3/2}} \cdot e^{-\frac{(x-\xi)^2 + (y-\eta)^2 + (z-\zeta)^2}{4k^2t}}.$$

* Gouy, *Ann. de chim. et de phys.* (5) xviii. p. 1 (1879).

For a medium extending in all directions, this expression gives the existing temperature at any place x, y, z , at any time t , if a definite amount of heat has been instantaneously introduced at the position ξ, η, ζ at the time $t=0$. The constant C is proportional to the instantaneous quantity of heat introduced.

Let us now consider a point in the medium on the z -axis, and at a distance ζ from the origin. As it passed the origin, heat was instantaneously introduced into this point, and the resulting distribution of temperature in the medium can be calculated from the above by putting $\xi=\eta=0$, and $\zeta=ct$. This gives

$$\begin{aligned} \mathfrak{S} &= \frac{C}{t^{3/2}} \cdot e^{-\frac{r^2 + y^2 + (z-\zeta)^2}{4k^2t}} = \frac{C}{t^{3/2}} \cdot e^{-\frac{r^2 - 2\zeta z + \zeta^2}{4k^2t}} \\ &= \frac{C}{t^{3/2}} \cdot e^{\frac{\zeta z}{2k^2}} \cdot e^{-\frac{r^2}{4k^2t} - \frac{\zeta^2}{4k^2}}. \end{aligned}$$

If we integrate this from $t=0$ to $t=\infty$, we obtain the solution of the problem, at first in the form :

$$\mathfrak{S} = C e^{\frac{\zeta z}{2k^2}} \int_0^\infty e^{-\frac{r^2}{4k^2t} - \frac{\zeta^2}{4k^2}} \cdot \frac{dt}{t^{3/2}} = -2C e^{\frac{\zeta z}{2k^2}} \int_0^\infty e^{-\frac{r^2}{4k^2t} - \frac{\zeta^2}{4k^2}} \cdot d\left(\frac{1}{\sqrt{t}}\right).$$

By the substitution of $\frac{1}{\sqrt{t}} = x$, we arrive at a known integral, namely,

$$\int_0^\infty e^{-p^2x^2 - \frac{q^2}{x^2}} \cdot dx = \frac{\sqrt{\pi}}{2p} e^{-2pq}.$$

We thus have :

$$-\int_0^\infty e^{-\frac{r^2}{4k^2t} - \frac{\zeta^2}{4k^2}} \cdot d\left(\frac{1}{\sqrt{t}}\right) = \int_0^\infty e^{-\frac{r^2x^2}{4k^2} - \frac{\zeta^2}{4k^2x^2}} \cdot dx = \frac{k\sqrt{\pi}}{r} \cdot e^{-\frac{\zeta r}{2k^2}},$$

and finally, if for brevity we set the constant magnitude $2Ck\sqrt{\pi} = A$,

$$\mathfrak{S} = 2Ck\sqrt{\pi} \cdot \frac{1}{r} \cdot e^{\frac{\zeta z}{2k^2}} \cdot e^{-\frac{\zeta r}{2k^2}} = \frac{A}{r} \cdot e^{\frac{\zeta}{2k^2}(z-r)}.$$

The isothermal surfaces are thus surfaces of rotation about the z -axis, since a definite temperature corresponds to every pair of values of z and r .

The following results are obtained from the discussion of the final equation

$$\mathfrak{S} = \frac{A}{r} \cdot e^{\frac{c}{2k^2}(z-r)} \quad \dots \quad (1)$$

At the origin ($r=0$), $\mathfrak{S} = \infty$;

along the positive z -axis ($z=r$), $\mathfrak{S} = \frac{A}{r}$;

along the negative z -axis ($-z=r$), $\mathfrak{S} = \frac{A}{r} \cdot e^{-\frac{c}{k^2} \cdot r}$; and

in the xy -plane ($z=0$), $\mathfrak{S} = \frac{A}{r} \cdot e^{-\frac{c}{2k^2} \cdot r}$.

If in the plane $z=z'$, which is parallel to the xy -plane, a definite temperature exists at the distance $r=r'$ from the origin, and the same temperature in the plane $z=z''$ at the distance $r=r''$, it follows from

$$\frac{A}{r'} \cdot e^{\frac{c}{2k^2}(z'-r')} = \frac{A}{r''} \cdot e^{\frac{c}{2k^2}(z''-r'')}$$

that
$$k^2 = \frac{c}{2} \cdot \frac{(z''-z')-(r''-r')}{\log \frac{r''}{r'}} \quad \dots \quad (2)$$

If we seek for points of equal temperature along the negative z -axis and in the xy -plane, and find them at the distances r_1 and r_2 from the origin (*e. g.* in the points A and B), we then have

$$\frac{r_2}{r_1} = e^{\frac{c}{k^2} \left(r_1 - \frac{r_2}{2} \right)}$$

and
$$k^2 = c \cdot \frac{r_1 - \frac{r_2}{2}}{\log \frac{r_2}{r_1}} \quad \dots \quad (3)$$

If k^2 is small and c is large, the values of $(z''-z')-(r''-r')$ and $\left(r_1 - \frac{r_2}{2}\right)$ approach zero, or $(r''-z'')=(r'-z')=\text{const.}$ and $r_2=2r_1$, *i. e.* the isothermal surface approximates to the form of a paraboloid of rotation, the focus of which lies at the origin, and of which the parameter converges towards zero for $c=\infty$. The point of equal temperature lies at

infinity along the positive z -axis. If the velocity of flow diminishes, the distance of this point becomes finite, and, provided U remains the same, the lower part of the surface surrounding the origin becomes broader. Finally, for $c=0$, we have $r_1=r_2$, and the isothermal surface becomes a sphere.

The application of these considerations to the present phenomenon of diffusion is obvious. The isothermal surfaces correspond to surfaces of equal partial pressure or of equal density, and from what has been said above, equation (1) is nothing else than the equation of the surface which encloses the sodium vapour developed from the glass bead. The shape of this surface varies according to the velocity of flow of the gas. Could we reduce the velocity to zero, then the surfaces of equal density would be spheres surrounding the bead. The limit of visibility would be distant and badly defined, corresponding to the low density gradient at the boundary. If, on the contrary, the velocity of flow were very great, the surface would take the form of a paraboloid of rotation, with the bead at its focus and with a well-defined boundary, especially in those parts near the bead which are advancing against the flow of the gas and where the density gradient at the limit of visibility attains very high values. The edges of the luminous figure beyond the bead are, however, more and more diffuse, and in the direction of the positive z -axis the figure extends theoretically to infinity. Between these two limits there exist all the forms between sphere and paraboloid, each of these forms corresponding to a certain value of the velocity of flow, although, of course, not all of them can actually be observed in the flame of a Bunsen burner, since the flame strikes back into the tube if the velocity sinks below a certain fairly high value.

We shall now give a calculation of the density gradient at each point of the surface of the luminous space, this gradient, taken normal to the surface, being a measure of the definiteness of the limit of visibility. We have, generally,

$$\frac{\partial \vartheta}{\partial n} = \sqrt{\left(\frac{\partial \vartheta}{\partial r}\right)^2 + 2 \frac{\partial \vartheta}{\partial r} \frac{\partial \vartheta}{\partial z} \frac{z}{r} + \left(\frac{\partial \vartheta}{\partial z}\right)^2}.$$

By means of equation (1) we obtain, putting $\frac{r}{2k^2} = B$,

$$\frac{\partial \vartheta}{\partial n} = -\frac{A}{r^2} e^{B(z-r)} \sqrt{1-2B(1+Br)(z-r)}.$$

On the surface, $\mathfrak{S}$ has a constant value K . Hence in the direction of the positive z -axis ($z=r$),

$$\frac{\partial \mathfrak{S}}{\partial u} = -\frac{A}{r^2} = -\frac{K}{r},$$

and in the direction of the negative z -axis ($-z=r$),

$$\frac{\partial \mathfrak{S}}{\partial u} = -\frac{A}{r^2} e^{-2Br} (1 + 2Br) = -\frac{K}{r} (1 + 2Br).$$

In the xy -plane ($z=0$),

$$\frac{\partial \mathfrak{S}}{\partial u} = -\frac{A}{r^2} e^{-Br} \sqrt{1 + 2Br + 2B^2 r^2} = -\frac{K}{r} \sqrt{1 + 2Br + 2B^2 r^2}.$$

From this we can deduce that the distinctness of the edges and the definiteness of the limit of visibility are greatest in the parts of the surface nearest the bead, and that they diminish with the distance from it.

The preceding theory was developed by the present writer, and a set of experiments carried out without knowledge of the previous work of H. A. Wilson. By using formula (2) and measuring the velocity of flow of the flame gases above the cone by a method due to Andrade*, values of k^2 were obtained which agree very well with those given by Wilson. Becker†, however, disputes the accuracy of this method, and points out that measurements by Jessel and later by himself and Laub‡, carried out by a photometric method, gave much smaller values (for sodium vapour 1.0 against 12 cm.²/sec.). It cannot be denied that there exists an uncertainty in the judgment of the light boundary of the luminous figure, and with velocities of flow as are rendered necessary to keep the flame from striking back into the tube, and for values of $k^2 < 5$ cm.²/sec. the deviations from the paraboloid form are already so small that the measurements become very uncertain. But for values as high as 12 or even 20 cm.²/sec. (in coal-gas-air flames of highest temperature), one can measure mean deviations from the paraboloid in quite a sure way. So the discrepancy remains to be explained.

§ 2. Anyone who observes the phenomenon investigated above will be struck by the similarity it bears to the appearance

* *Ann. d. Phys.* xxxvii. p. 380 (1912).

† *Phil. Mag.* xxiv. p. 707 (1912).

‡ Heidelberg, *Akad. Ber.* (1911).

of a comet in the neighbourhood of the sun. However doubtful it may seem in general to deduce innate relations from similarity, it is perhaps permissible briefly to indicate that this similarity might be more than simply a formal one.

The nucleus of a comet contains carbon, and it has been shown by spectral analysis that, in consequence of heating by the sun's rays, hydrides of carbon and carbon monoxide are developed from this carbon in the immediate neighbourhood of the sun, and sometimes also sodium- and iron-vapour. But according to the work of Schwarzschild * and of Debye † it is impossible, leaving aside for the moment the case of resonance, that light-pressure exceeds the attraction of the sun for particles of such small diameter as molecules or atoms, even if they be assumed to be totally reflecting. On the contrary, radiation pressure is of negligible magnitude for particles of diameter so much smaller than the wave-lengths in which the sun emits its energy, and this in consequence of the diffraction of the light. In order to cope with this difficulty, it is well known that Arrhenius's theory of comets, which is based on radiation pressure, assumes that the gases ascending from the nucleus condense, and that it is the larger particles formed in this way which are acted on by light-pressure and which form the tail of the comet. But in this case it is very difficult to understand why in the comet's tail often the same characteristic *gas spectrum* is observed as is noted in the neighbourhood of the nucleus.

However, quite recently, Megh Nad Saha ‡ has developed very remarkable ideas about the gases which are raised to immense heights in the solar atmosphere, and this work seems to make it clear why, in the first place, the elements are by no means arranged according to their weights in the atmosphere of the sun. From amongst the known elements, calcium is elevated to the greatest height, in spite of its atomic weight, whilst on the other hand, light elements like boron and nitrogen are entirely absent in the solar spectrum. Saha explains this as due to the calcium atoms being strongly influenced by the light-pressure of the sun, in spite of their smallness, since at these high temperatures and low pressures the calcium becomes ionized by the emission of an electron, and is then rendered luminous by the solar radiation owing to resonance excitation, particularly when the wave-length

* Schwarzschild, *Sitzgsber. d. Akad. zu München*, xxxi. p. 293 (1901).

† Debye, *Ann. d. Phys.* xxx. p. 57 (1909).

‡ Saha, *Phil. Mag.* xl. p. 809 (1920).

corresponding to resonance lies in the region of the maximum of radiation of the sun. As a matter of fact, Schwarzschild's calculations refer to small reflecting spheres, and an absorption of radiation such as occurs in the case of resonance can give rise to a preponderance of light-pressure over gravitation even with particles of atomic magnitude, as has been noted previously by FitzGerald, Lebedew, and Debye.

Is it not plausible to assume that there is also gas in the sun's atmosphere which, for the same reason, is acted upon by light-pressure with such great intensity that the gas permanently leaves the sun? The green line ascribed to the hypothetical element coronium can be observed up to a height of 20 minutes from the edge of the sun, and the corona attains even to a distances of 6° to 7° , or several times the diameter of the sun. Pringsheim* has already remarked that in the case of the spectrum of the corona we might possibly be dealing with the fluorescence spectrum of a gas; and in support of this he mentions the "washed out" nature of the main line in the inner corona, and in the case of the outer corona the appearance of the continuous spectrum, which Lockyer describes as being crossed by numerous emission bands. From what we know about the fluorescence radiation of gases we may be concerned here with one and the same gas in the inner and outer corona, which is differently excited under different conditions (temperature, and admixture of foreign gases). Moreover, according to Saha's theory it is not necessary that this coronal gas should be particularly light; it need only be capable of resonance in the part of the solar spectrum which is rich in energy.

Whatever views we may hold as to the question of the limits of an atmosphere, it must certainly be admitted that a gas that has once been raised to such enormous heights by radiation pressure can also permanently leave the sun, for if the light-pressure is greater than the solar attraction it will remain greater, since both magnitudes and hence also their difference diminish with the square of the distance from the sun. Of course we are dealing here with extremely attenuated gas, the pressure of which, even in the corona, may lie far below that which can be obtained at present with the best vacuum pumps. With increasing distance from the sun this degree of attenuation will diminish still further, so that the motion of the planets will not be influenced in the least. Even Seeliger's theory of the zodiacal light, which

* Pringsheim, 'Physik der Sonne,' p. 319. Leipzig (Teubner), 1910.

attempts to explain the empirical terms in the motion of the inner planets, would permit a mean density of the zodiacal cloud such as could be attained by our vacuum pumps. Nevertheless, the number of atoms per cubic centimetre will still amount to thousands, even at great distances from the sun.

At the same time, one of the results of the high vacuum will be that the atoms, in consequence of the large free paths, will receive very considerable velocities in the radial direction by virtue of the preponderance of the pressure of the light, just as in the case of the ions of a rarefied gas under the action of an electric field. This velocity will diminish slowly with increasing distance from the sun, for although the propelling force falls off rapidly, the free paths increase at the same time as the rarefaction of the dispersed gas becomes greater. At present we can only say that the magnitude of the velocity might be very large. If it be so large that the atomic ions become positive atomic rays, so that we should have to identify them with the positive rays assumed by Vegard on the basis of the phenomena of the aurora, then of course the kinetic ideas here developed would have to be correspondingly modified, for in such a case the action on the gas of the comet would no longer be that of a simple impact.

It should be pointed out that the absence of the fluorescent light of the coronal gas, which on this view fills planetary space, could be explained by the enormous attenuation and by the diminution of the excitation, which is inversely proportional to the square of the distance from the sun. At the same time it is also possible that the almost continuous band spectrum of the coronal gas is not separable from diffuse daylight or diffuse stellar light owing to its feeble intensity, and that the spectrum of the zodiacal light which is at present simply described as being continuous may yet prove to be in part a band spectrum like that of the outer corona. It has often been maintained that there are relations between the corona and the zodiacal light.

When the comet enters this gas, which is streaming away from the sun with large velocity, the gases developed from its nucleus gravitate of themselves towards the sun, since they will not be excited to resonance, or at least not sufficiently. According to the experiments of Lebedew, the radiation pressure of sunlight on the molecules of acetylene is a thousand times smaller than the gravitational action of the sun. We must assume that, apart from the nucleus, the

density of the comet gases is exceedingly small, but that their temperature is not inconsiderable, even when we are not inclined to interpret their luminosity as of purely thermal origin. The gases of the comet then diffuse with almost molecular velocity into the upward stream of gas driven from the sun by radiation pressure, and the whole process will take place essentially according to the same laws, although at extremely small partial pressures, as were obtained above in the case of the sodium vapour developed from the glass bead. We have first the development of a spherical envelope at great distance from the sun, then a lagging behind of the envelope with respect to the nucleus as the distance from the sun diminishes, and finally the development of a parabolic envelope with the nucleus at its focus, in which case the diameter of the figure above the nucleus becomes smaller. These phases roughly represent the stages in the development of every large comet, and correspond exactly with what we should expect if the stream-velocity and the density of the gas increases, into which the vapours developed from the nucleus diffuse. The presence of a gas spectrum in the tail of the comet is then quite natural.

But, in addition, all the other essential features of the phenomenon of comets can be readily interpreted. This applies to the angles included between the tail and the prolonged radius vector in the plane of the orbit, and to its curvature from the proper-motion of the nucleus. Small angles which can also be included between the tail and the orbital plane are capable of interpretation from the fact that the emission of gas by the sun will be different according to direction and time, and the flow of gas can also obtain small lateral components in virtue of the equalisation of density which takes place in planetary space. The forces of repulsion often ascribed to the nucleus, and the repeatedly observed phenomenon of concentric envelopes one within the other, are explicable from the gradient of partial pressure and the different value of this gradient for the individual gases which are developed from the nucleus. The sharp boundary of the advancing edge of the tail and the diffuse boundary of the edges of the tail behind the nucleus can be explained by the much higher density gradient in the former place. Moreover, we can explain the three types of comet's tails proposed by Bredichin that can be occasionally observed even simultaneously on one comet, on the bases of the different velocity of the molecules and of diffusion of the gases

developed from the nucleus. Here, however, in contradistinction to Bredichin's view, we should have to assign Type I. (long and narrow tails) to the heavier gases and Type II. (short and broad tails) to the light gases, whereas Type III. (feeble tails occurring only in the neighbourhood of perihelion and directed towards the sun) would, in accordance with the general view, have to be interpreted as a dust-cloud formed by the very violent removal of the gas of the nucleus and consisting of coarser solid particles which fall towards the sun. The presence of this dust corresponding to vigorous activity of the nucleus has been established by the detection of reflected sunlight in the heads of comets near the sun. Doubtless the particles constituting this dust will possess all possible magnitudes, and it must be admitted that particles of suitable magnitude, for which light-pressure exceeds gravitation, can also enter into the tails of Types I. and II., which are directed away from the sun. But since here the luminous matter exists mainly in the state of gas, these particles will not decisively determine the form of these tails.

Should these conceptions appear too purely mechanical, and, in particular, if the luminosity of comets should later be recognized as a purely electrical phenomenon, the view developed here would have to be modified, in the sense that the atomic ions which leave the sun are accelerated by light-pressure until they attain the velocity of atomic rays. These rays then excite luminosity in the molecules of the gaseous envelope of the comet through which they pass, and impart to them in addition a certain velocity in the direction of flight, which is distributed over the whole gas of the comet and causes it to stream. Some time ago Vegard* endeavoured to explain the development and the gas nature of comets' tails in this manner, on the assumption of radioactive processes in the sun, however, as the source of the atomic rays.

According to both views, it is not light-pressure, at least not directly, which acts on the gases of the comet, but the action takes place through the agency of matter which is transmitted with large velocity away from the sun.

* *Ann. d. Phys.* xli. p. 641 (1913).

LXVIII. *Table of Values of the Integral* $\int_0^x K_0(t)dt$.

By S. P. OWEN, *Royal Grammar School, Newcastle-on-Tyne* *.

THE following tables were constructed for the purpose of an investigation in which occurred the integral

$$\int_0^x K_0(t)dt,$$

the function $K_0(t)$ being the modified Bessel function of the second kind of order zero.

Since no tables of this integral, nor of the modified Struve function, have been computed previously, it may be of interest to set such tables on record.

The integral $\int_0^x K_0(t)dt$ is expressible in the form †

$$\frac{1}{2}\pi x \{ I_0(x) K_1(x) + L_0'(x) K_0(x) \},$$

where ‡
$$L_0 = \sum_{m=0}^{\infty} \frac{(\frac{1}{2}x)^{2m+1}}{\Gamma(m + \frac{3}{2})^2},$$

$L_0'(x)$ is the derivate of $L_0(x)$, and $K_1(x)$ is Macdonald's form of the modified Bessel function of order unity.

From these results the tables were computed with the help of seven-figure logarithm tables, and so they may be taken as accurate to five significant figures.

When x is large $L_0(x) \sim I_0(x)$, where $I_0(x)$ is the modified Bessel function of the first kind, while

$$\lim_{x \rightarrow \infty} \int_0^x K_0(t)dt = \frac{\pi}{2}.$$

The last formula is a special case of results quoted by Watson (*loc. cit.* p. 388).

x .	$L_0(x)$.	$L_0'(x)$.	$\int_0^x K_0(t)dt$.
0.02	0.01273296	0.6367046	0.1005627
0.1	0.0637327	0.638743	0.3421645
0.5	0.3272407	0.690562	0.9271025
1	0.710243	0.863384	1.242509
2	1.937433	1.739380	1.473676
3	4.64741	4.033232	1.539706
4	11.13105	9.79822	1.560113
5	27.10592	24.36484	1.567387
6	67.1245	62.2126	1.569635
7	168.5005	156.0532	1.570402
8	427.4832	399.884	1.570658
9	1093.516	1030.92	1.570747
10	2815.632	2670.995	1.570779
11	7288.43	6948.87	1.570790
12	18948.84	18141.25	1.570794

* Communicated by Prof. G. N. Watson, F.R.S.

† Cf. Watson, 'Theory of Bessel Functions,' 1922, p. 752.

‡ *Ibid.* p. 329.

LXIX. *Electrical Properties of Helium.* By J.S. TOWNSEND, M.A., Wykeham Professor of Physics, Oxford, and S. P. MCCALLUM, B.A., Rhodes Scholar, Hertford College, Oxford*.

THE experiments on the photoelectric currents in helium between parallel plate electrodes, arranged in a manner to determine the rate of increase of the current with the distance between the plates, have shown that the electrons set free from the negative electrode by ultra-violet light acquire sufficient energy to ionize molecules by collision before any other process of ionization takes place to an extent which is appreciable in comparison with the effect of ionization by single collisions.

The principal evidence in support of this conclusion consists in the fact that for a certain range of distance between the plates, when the electric force X and gas-pressure p are constant, the currents are in accurate agreement with the formula $n = n_0 e^{\alpha x}$, and the values of α as found experimentally are given in terms of X and p by an equation of the form $\alpha/p = f(X/p)$.

Some interesting results with regard to the energy required to ionize a molecule, and the loss of energy of electrons in collisions with molecules which are not ionized, may be deduced from these experiments by simple calculations which do not involve the mean free paths of the electrons.

These results, however, are not in agreement with the properties of atomic models as indicated by the quantum theory which are considered by some physicists to be satisfactorily established by experiments arranged on the principle of Lenard's method of determining ionizing potentials where the electrons pass through two or more spaces between grids at various potentials. The experiments of this type have been interpreted as showing that there is a series of critical potentials V_1 , V_2 , &c. called resonance potentials, which represent the loss of energy of electrons when they collide with molecules with velocities exceeding the velocity corresponding to one of the resonance potentials. The resonance potentials correspond to wave-lengths in the ultra-violet spectrum, and when the radiation from the molecules falls on an electrode, electrons are set free.

The resonance potentials are less than the ionizing

* Communicated by the Authors.

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potential V_i , so that in cases where electrons are set free from a metal surface with a small velocity and make several collisions with molecules when they move under an electric force through a gas, they would lose their energy in producing resonance effects before attaining the energy corresponding to the ionizing potential. Under these circumstances no appreciable number of molecules would be ionized by collisions. If this be a correct representation of the effects produced by collisions, it would be necessary to assume that the increases in the current obtained by increasing the distance between the electrodes in the parallel plate experiments are due principally to electrons set free from the negative electrode by radiation from the molecules of the gas. A formula for the rate of increase of the current with the distance between the plates which would arise from this process is easily obtained, and it gives values for the currents which differ by such large factors from those observed experimentally, that it is impossible to reconcile the radiation theory with the parallel plate experiments.

Since widely different views are taken as to the effects produced by the collisions of electrons with molecules, it was considered desirable to investigate the conductivity of gases by another method, in order to decide by direct experiment whether there are any additional electrons set free from the negative electrode by radiation from molecules of the gas, using potentials and gas-pressures as in the parallel plate experiments where the current increases with distances between the plates in accordance with the formula $n = n_0 e^{ax}$.

2. In order to show the ranges of forces and pressures to be adopted in this investigation, it is necessary to give the results of some experiments with the simple form of parallel plate apparatus which has hitherto been generally used. The electrodes were silver plates 6 cm. in diameter, and the conductivity was obtained by the action of ultra-violet light from an external spark-gap, which set free electrons from the negative electrode. The precautions taken to eliminate impurities were the same as those described in the accounts of other experiments with helium which were made in the laboratory.

The results of the experiments with helium at four different pressures (19, 10, 6, and 4 millimetres) are given in Table I. In the experiments at each pressure the distance between the plates was increased in steps of one millimetre from 5 to 10 millimetres, and the currents for the six different distances were measured, using the same electric force of 120 volts per centimetre. The first two lines of figures in

the table give the distances x between the plates in centimetres and the potential V between the plates in volts. The currents i obtained experimentally are given in arbitrary units, taking 100 as the value of the current with the plates at 5 millimetres apart. The values of α were deduced from the ratios of the currents at the shorter distances, and the quantities $n_0\epsilon^{\alpha x}$ are given immediately below the corresponding currents, the constant $n_0\epsilon^{\alpha \times 5}$ being taken as 100.

TABLE I.

x	5	6	7	8	9	10
V	60	72	84	96	108	120
$p=19$ mm.						
i	100	136	187	250	337	455
$\alpha=3.05$						
$n_0\epsilon^{\alpha x}$	100	127	184	250	338	460
$p=10$ mm.						
i	100	138	198	275	405	615
$\alpha=3.46$						
$n_0\epsilon^{\alpha x}$	100	142	200	283	400	566
$p=6$ mm.						
i	100	142	202	292	440	675
$\alpha=3.57$						
$n_0\epsilon^{\alpha x}$	100	143	204	292	416	596
$p=4$ mm.						
i	100	140	196	276	426	700
$\alpha=3.37$						
$n_0\epsilon^{\alpha x}$	100	140	196	275	385	540

Allowing for an experimental error of about 2 per cent., it is seen that the currents are in agreement with the formula within certain ranges of potential. With the pressure 19 millimetres, the ratio X/p being 6.31, the agreement extends up to a potential of 120 volts. The range diminishes with the pressure, as shown by the figures in the last column where the values of i are much greater than the quantities $n_0\epsilon^{\alpha x}$ with the pressures 10, 6, 4 millimetres. At the lowest pressure, 4 millimetres, where the ratio X/p is 30, the limit of the range of potential where the currents are in agreement with the formula is between 96 and 108 volts, but there is no abrupt change to indicate the exact limit of the range.

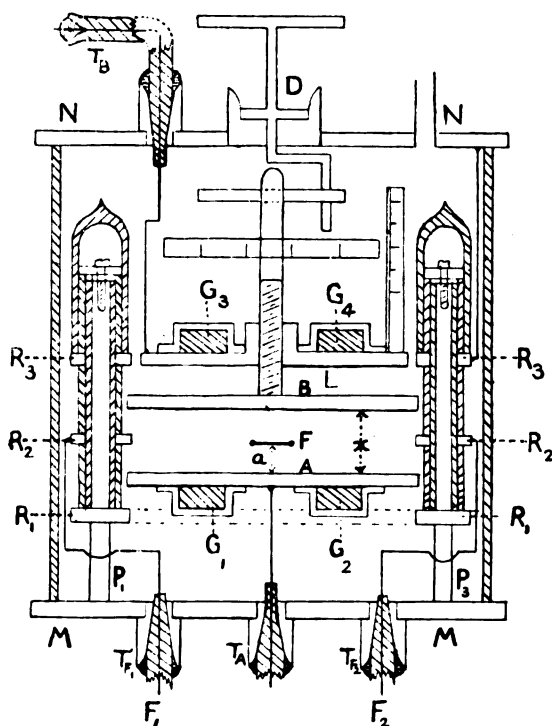
3. These experiments have been interpreted as showing that the increase of the conductivity of the gas with the distance between the plates is due to ionization of molecules of the gas by the collisions of electrons when the currents increase with the distance in accordance with the formula $n_0 e^{ax}$, and that there is no appreciable effect due to any other process of ionization under these circumstances.

With larger distances between the plates, where the rate of increase of the current with the distance exceeds the rate of increase of the quantity $n_0 e^{ax}$, some additional process of ionization begins to produce an appreciable effect. This effect may be due to ionization of molecules by the collisions of positive ions, or to electrons set free from the negative electrode by the impacts of positive ions, or to electrons set free from the electrode by radiation from molecules of the gas. For the purpose of this investigation it is not necessary to decide which of these processes is the most important. They have some features in common which make it possible to obtain direct experimental evidence in support of this theory by measuring the currents obtained in a modified form of apparatus with two parallel plates.

4. The method of investigation which has been adopted for this purpose, involves the measurement of the currents to the two plate electrodes A and B (shown in fig. 1). The electrodes were 8.8 cm. in diameter and were plated with silver. A short filament F of fine platinum wire was set up between them at a fixed distance (a) from the lower plate A. The upper plate B was mounted on an axle with a micrometer screw so that it was possible to adjust the distance x between the two plates to any length from 10 to 18 millimetres. The distance a of the filament from the lower plate was 7 millimetres. The filament was supported by two fine silver wires (as shown in fig. 2), which also lay in the plane at 7 millimetres from the lower plate.

The insulators were of glass, and are shaded in the diagram (fig. 1) to distinguish them from the metal parts which were made of silver-plated brass. The apparatus was enclosed in a glass cylinder, cemented to the metal base M and to the top cover-plate N. The brass ring R_1 was fixed to the base by four short brass rods, two of which, P_1 and P_3 , are shown in the diagram. Four longer rods formed continuations of the short rods to carry the rings R_2 and R_3 , from which they were insulated by sleeves of glass tubing. The sleeves fitted the rods and passed through holes in the rings. The rings R_2 and R_3 were held in position parallel to the ring R_1 by

Fig. 1.



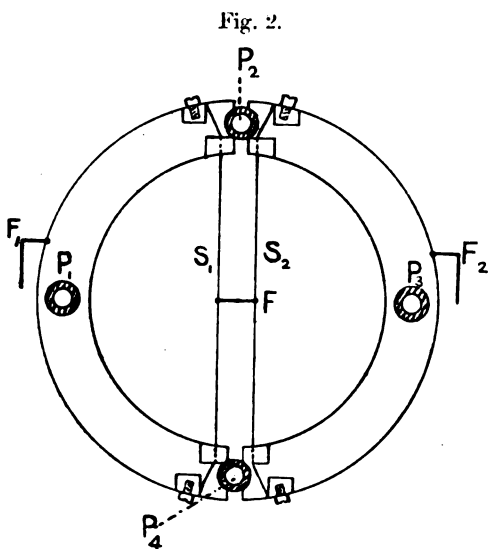
The micrometer screw carrying the plate B was rotated

by the axle D resting on a flat bearing in the cover-plate, and the bearing was made air-tight with tap-grease.

The connexion to the plate A was made through a long glass capillary tube T_A ground to fit a tapered brass socket in the base, and was made air-tight by cement on the outside.

The connexion to the plate B was made in a similar manner through the cover-plate N by the capillary tube T_B .

The ring R_2 was split along the diameter through the rods P_2 and P_4 , as shown in fig. 2. Two silver wires, S_1 and



S_2 , were stretched tightly between the ends of the sections at seven millimetres apart, and the platinum filament F was soldered to the silvered wires. The connexions to the sections of the ring were made through the wires F_1 and F_2 , which carried the heating current. These wires passed through insulating glass tubing fitted into sockets in the base, as shown in fig. 1.

5. In each experiment the lower plate A was at zero potential, the filament was maintained at a potential V by a battery of small accumulators, and the upper plate B was charged to the potential Vx/a . A uniform electric force X was thus established in the field between the two plates, except in a small space near the filament and the silver wires where the uniformity of the field of force is disturbed

by the surface distribution on the wires. There is no appreciable change in the distribution of the electric force near the filament when the distance x is changed from x_1 to x_2 and the potential of the upper plate changed from Vx_1/a to Vx_2/a . The latter potentials were carefully adjusted with a potentiometer, as it was found that there was a large change in the number of electrons passing from the filament to the lower plate A due to a small change in the potential of B. The investigation of the properties of the conductivity considered in section 3 depends on measurements of the ratio of the currents to the plates A and B, and is not affected by small errors in the adjustment of the potential of the plate B. It is, however, of advantage to adjust these potentials accurately, in order to represent the currents by continuous curves in terms of the potential V .

The filament was heated to a dull red by a battery of large accumulators, and the current was maintained for a considerable time until the electron emission became constant. The fall of potential between the terminals leading to the filament was about a quarter of a volt, so that no appreciable error is introduced in taking the potential of the filament and the wires supporting it as being at the potential V of the centre of the filament.

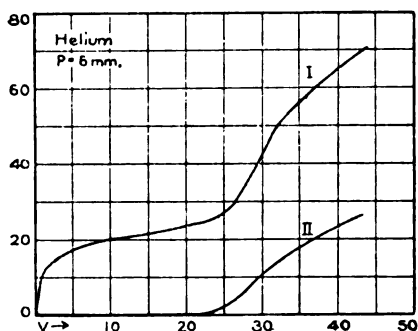
The currents to the plates were found by a zero method with an induction balance, so that when the plates were insulated their potentials did not change by more than a small fraction of a volt while the currents which they received through the gas were being measured. A sensitive quadrant-electrometer was used as the indicator in connexion with the balance, and small emission currents from the filament were used in order to avoid any disturbance of the field by the charges of the electrons or positive ions in the space between the plates. The relative values of the currents obtained with different forces were, in all cases, independent of the intensity of the filament emission.

6. When the potentials V and Vx/a of the filament and the upper plate are negative, a stream of electrons flows to the lower plate and, with large potentials, the upper plate receives a positive current. The currents flowing to the two plates were measured with a constant filament emission and a constant distance of 12 millimetres between the plates for different fields of force obtained by altering the potentials of the filament and upper plate, the potential of the latter being adjusted to $12V/7$ when the filament was at the potential V .

The currents obtained with helium at a pressure of

6 mm. are represented by the curves (fig. 3) in terms of the potential V of the filament, the ordinates of Curve I. being the negative currents through the gas to the lower plate, and the ordinates of Curve II. the positive currents to the upper plate. The currents were obtained in the ordinary manner by making a series of observations of the quantities of electricity received by the plates in equal intervals of time. The induction balance was adapted to measure the charges received by the two plates during the same interval of time. The ratio of the two currents was thus obtained very accurately, since by this method there is no error due to fluctuations in the filament emission. The ratios thus found were in good agreement with the ratios of the ordinates of the two current electromotive force curves given in fig. 3.

Fig. 3.



Curve I. shows that there is a small increase in the negative current to the lower plate as the potential V is increased from 10 to 20 volts, due to additional electrons from the filament, and a large increase due principally to some process of ionization in the gas with the larger forces from 20 to 40 volts. Curve II. leads to the same conclusion, as the positive current to the upper plate is very small (due to a small positive emission from the filament), while V is less than 20 volts, but increases rapidly with the larger values of V .

7. The point to be decided is whether the increases in the currents obtained when V is increased from 20 to 40 volts can be attributed to any cause except the direct ionization by the collisions of electrons with molecules in the space between the filament and the lower plate. For example, let it be supposed that the electrons emitted from the filament excite radiation in colliding with molecules in the space

between the filament and the lower plate, and that this radiation sets free electrons from the upper plate. Let n_1 be the number of electrons emitted from the filament n_2 the corresponding number set free from the upper plate by the radiation excited by the electrons from the filament. The electrons thus set free from the upper plate also collide with molecules, and by a similar process the number n_2 becomes multiplied to rn_2 , and the total effect corresponding to any value of V from 20 to 40 volts is represented by the ordinate of Curve II. (fig. 3). The action is now exactly similar to that observed in the simple case of parallel-plate electrodes when ultra-violet light from an external spark-gap falls on the negative electrode, and the experiments recorded in Table I. show that large increases in the factor r may be obtained when the electric force and gas-pressure are constant and the distance between the plates is increased.

If the distance between the plates be increased from 12 to 17.5 millimetres and the potential of the upper plate increased from 12 V/7 to 17.5 V/7 when the filament is at the potential V , the curves, fig. 3, would assume a different form. While the ordinates from $V=10$ to $V=20$ remain constant, the ordinates of both curves from $V=20$ to $V=40$ would be increased. The change to be expected may be found by considering the ordinate of Curve II. at the point corresponding to $V=40$. At this point the potential of the upper plate is 68.5 volts when $x=12$ mm. and 100 volts when $x=17.5$ mm., thus the increase in distance involves an increase of 31.5 volts in the potential difference between the plates. The ordinate of Curve II. would therefore be increased by a factor of 2 at least, since the experiments recorded in Table I. show that the current is increased from i to $2i$ approximately when the distance between the plates is increased by an amount involving an increase of 24 volts in the potential difference between the plates. Thus the radiation hypothesis leads to a conclusion which differs widely from that indicated by the theory of ionization by collision.

According to the latter theory, the increases in the current with the potential V are due to the ionization of molecules in the space between the filament and the lower plate, and the rate of increase of the current with the potential would not be affected by increasing the distance between the plates, provided the total potential difference between the plates does not exceed 100 volts and the pressure of the gas is above 3 millimetres. This limit of pressure is indicated by the third experiment in Table I., where $X/p=20$, if the

effect of the increase of temperature of the gas due to the filament be neglected.

8. Experiments were therefore made with the apparatus shown in fig. 1, the distance between the plates being 17.5 mm. instead of 12 mm., and it was found that with the gas at 6 mm. pressure the two curves representing the currents to the lower and upper plates with $x=17.5$ mm. were precisely the same as those given in fig. 3 for the distance $x=12$.

The experiments were repeated several times with gas that had been used in the apparatus for some days and with a fresh supply of gas that had been kept for a few hours in a charcoal tube cooled with liquid air, and no change was observed in the rate of increase of the current to either plate with the potential V when the distance between the plates was changed from 12 to 17.5 millimetres, the maximum potential difference between the plates being 100 volts. These experiments were made with pressures of the gas from 4 to 20 mm.

Under these conditions, therefore, it must be concluded that there is no effect due to electrons set free from the negative electrode by radiation from molecules of the gas which is comparable with the effect of direct ionization by the collisions of electrons with molecules of the gas.

It is also easily seen that the positive ions make no appreciable contribution to the conductivity in these experiments either by ionizing molecules of gas or by setting free electrons from the negative electrode, for in these processes of ionization the action would be increased by increasing the distance between the electrodes as in the case of radiation.

9. The collision theory explained in section 3 receives further support when larger potential differences are used between the plates A and B (fig. 1). In the experiments with the photoelectric currents recorded in Table I. where the rate of increase of the current with the distance x exceeds the rate of increase of the quantity $n_0 e^{ax}$, the change in the mode of development of the current has been attributed to one of three processes. In the second experiment (Table I.), where the gas was at 10 millimetres pressure, the distance between the plates one centimetre, and the potential $V=120$ volts, the effect of the additional process of ionization is shown by the divergence between the figures 615 and 566.

In experiments of this type it has been found that the divergence from the formula obtained with a given potential difference V depends only on the ratio X/p . Thus if the

force were 60 volts per centimetre and the pressure 5 millimetres, the current with a distance of 2 centimetres between the plates would exceed the corresponding quantity $n_0 e^{ax}$ by the same factor 615:566.

The experiments given in the table may therefore be taken as showing that with a potential difference between the plates of 96 volts there is no additional process of ionization at any pressure for which the ratio X/p is less than 30. With 120 volts there is a distinct effect when $X/p=12$, which becomes more marked as the ratio X/p increases. When $X/p=30$ a distinct additional effect is obtained with the potential 108 volts, as shown by the experiments with the gas at 4 millimetres pressure.

In experiments with the arrangement of electrodes shown in fig. 1 where the filament is 7 millimetres from the lower plate, the electric force is 68.5 volts per centimetre when the potential of the filament is 48 volts, the upper plate being at 82 volts when $x=12$ and at 120 volts when $x=17.5$. The above theory therefore shows that with $x=12$ millimetres and the gas-pressure above 2.3 millimetres, the increases in the currents to the electrodes obtained by increasing the potential of the filament from 10 to 48 volts are due to ionization by collision of electrons with molecules of the gas, no other process of ionization having an appreciable effect. With $x=17.5$ millimetres an additional process of ionization should be appreciable with the larger forces, and the effect should become more marked as the pressure is reduced.

10. The results of the experiments with the larger forces are shown by the curves (figs. 4 & 5). With the gas at 10 millimetres pressure and the plates 12 millimetres apart, the currents to the lower and upper plates (A and B, fig. 1) are given by the curves i_1 and i_2 (fig. 4). With the gas at the same pressure and the plates 17.5 millimetres apart the currents are given by the curves i'_1 and i'_2 . The curve i_1 coincides with the curve i'_1 and i_2 with i'_2 for potentials of the filament less than 48 volts. With the filament at 55 volts the currents corresponding to $x=17.5$ are greater than those for $x=12$. In these experiments ($p=10$ mm.) when $V=48$ volts, the value of X/p is 6.85 and the potential difference between the plates is 120 volts with $x=17.5$. The absence of any additional process of ionization up to this point is in agreement with the theory of the photoelectric currents recorded in the first experiment (Table I.), where $X=120$ volts per centimetre and $p=19$ millimetres, X/p being 6.3.

Fig. 4.

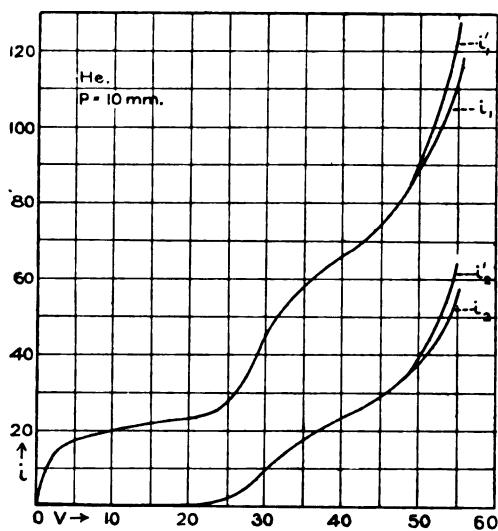
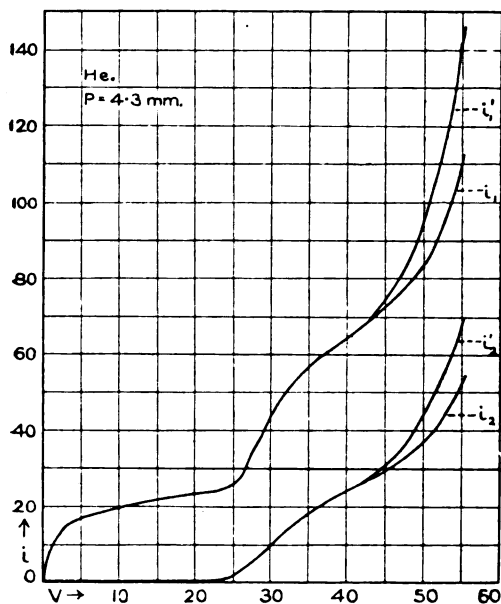


Fig. 5.



The figures in Table I. indicate that all additional processes of ionization are absent up to a higher point with smaller values of the ratio X/p . This was found to be the case with the filament currents through the gas at 20 millimetres pressure. The currents to the lower and upper plates for all potentials V of the filament up to 55 volts were the same for the two distances between the plates $x=12$ and $x=17.5$ millimetres, the potential difference between the plates being 137 volts when $x=17.5$ millimetres and $V=55$ volts.

With pressures less than 10 millimetres the curves representing the currents to the two plates for the two distances $x=12$ millimetres and $x=17.5$ millimetres are more divergent, and the divergence occurs with smaller values of V than is indicated by the curves (fig. 4).

With the gas at 6 mm. pressure there was a distinct increase in the currents to both plates with the filament at 48 volts, due to changing x from 12 to 17.5 millimetres.

With the gas at 4.3 mm. pressure the increase in the currents to the two plates due to changing x from 12 to 17.5 millimetres was much more marked. The values of i_1 and i_2 corresponding to $x=12$, and i'_1 and i'_2 corresponding to $x=17.5$, are given by the curves (fig. 5).

The experiments show that the additional process of ionization which causes the divergence between the curves (figs. 4 & 5) rises in importance as the value of X/p increases, in the same way as the values of the current i exceed the quantity $n_0 e^{ax}$ in the experiments with the photoelectric currents recorded in Table I. It would be difficult to obtain evidence of an exact agreement between the two methods of indicating the points at which the additional process of ionization becomes appreciable, as this would involve an estimate of the rise of temperature of the gas due to the heated filament, and of the action of the wires supporting the filament in intercepting electrons and positive ions in the space between the plates.

It is of importance, however, to show that the rate at which molecules are ionized by the collisions of electrons is the same in the photoelectric and thermionic currents, but for this purpose it is better to consider the currents obtained with the heated filament when the electric force is reversed and the stream of electrons from the filament traverses different distances $(x-a)$ through the gas to the upper plate B (fig. 1).

11. The preceding investigation does not indicate the exact cause of the additional ionization, except that it cannot

be attributed to a photoelectric action of radiation from molecules of the gas of the type which has been suggested. If the molecules emit radiation in consequence of the collisions of electrons moving with velocities corresponding to a series of resonance potentials, V_1, V_2 , &c., less than the ionizing potential V_i but of the same order, the photoelectric effect of the radiation should rise and fall with the pressure when the electric force is constant approximately in the same manner as the quantity α varies with pressure in the experiments given in Table I. These experiments show that α diminishes as the pressure is reduced from 6 to 4 millimetres, but the additional process of ionization which causes the currents to exceed the quantity $n_0 e^{ax}$ rises in importance. Since the effect increases continuously with the large values of the ratio X/p , it appears to be due to positive ions which become more active as their velocity increases, or to radiation excited by collisions of electrons when moving with velocities much greater than that required to ionize molecules of the gas.

The remarkable feature of this action is that it is so large in the monatomic gases. In helium it is appreciable in currents between parallel plates when the potential difference between the plates is 108 volts and the ratio X/p is 30. In hydrogen when the ratio X/p is 88, the corresponding effect does not become appreciable until the potential difference between the plates is 200 volts.

It is probable that the action is due to positive ions which acquire more energy in helium than in hydrogen under the action of an electric force, as the loss of energy of the ions in collisions with molecules which are not ionized would be less in monatomic than in diatomic gases. The collisions of a positive ion with molecules which are not ionized may be supposed to resemble the collisions of a molecule (A) which had acquired a large energy of translation exceeding the energy of translation of the surrounding molecules. In monatomic gases the molecule (A) loses energy in collisions owing to the transfer of momentum, but in diatomic gases energy is lost both by the transfer of momentum and the conversion of energy of translation into energy of rotation.

12. In the papers describing the results of previous experiments with helium, it has been shown that the large effects due to ionization by the collisions of electrons with molecules cannot be explained on the hypothesis that a molecule is "partially ionized" by one collision and complete ionization is obtained by a second collision. Also, with the photoelectric currents, the fact that the activity of

the electrons is independent of the intensity of the ultra-violet light from the external spark-gap indicates that this light does not affect the molecules of the gas.

It has however been suggested that even with light of small intensity the molecules may become "partially ionized," and the large effects obtained by single impacts of electrons with molecules may be due to this cause.

In view of this objection, it was considered desirable to find the activity of the electrons from measurements of the conductivity obtained by means of a heated filament, and to compare the result with the activity found in the experiments where electrons are set free from the negative electrode by ultra-violet light from an external spark-gap. The small currents suitable for this purpose are obtained when the filament is heated to a dull red so that there are no rays from the filament which can affect the molecules of the gas.

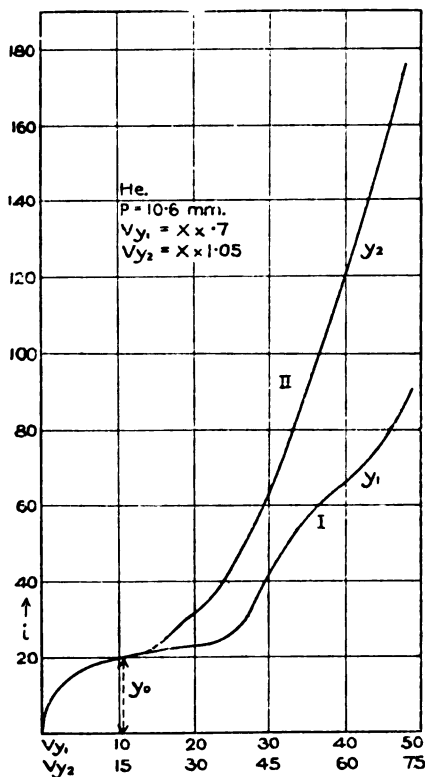
It is difficult to find the rate at which molecules are ionized from a curve representing the current in terms of the potential difference between the electrodes such as Curve I. (fig. 3), since the increase of the current with the potential is due partly to additional electrons coming from the filament. This difficulty is avoided by reversing the electric force and measuring the currents of electrons to the upper plate B (fig. 1) when it is set at two different distances $(x_1 - a)$ and $(x_2 - a)$ from the filament. The temperature of the filament is affected by varying the distance between the plates so that it is necessary to measure the currents y_1 corresponding to different forces X with the upper plate at a fixed distance $(x_1 - a)$ from the filament, and after changing the distance to $(x_2 - a)$ and adjusting the temperature of the filament, to measure the currents y_2 corresponding to the same electric forces. The currents y_1 with the plate B at 7 mm. from the filament are given by Curve I. (fig. 6); the currents y_2 with the plate B 10.5 mm. from the filament are given by Curve II., the electric force X being in volts per centimetre, and the gas-pressure 10.6 mm.

The same ordinate $y_0 = 20$ is taken to represent the current with the lowest force in each curve. The difference between the ordinates $(y_2 - y_1)$ corresponding to a large force X represents the number of molecules ionized in the space between the two planes x_1 and x_2 , and y_1 the number entering the space. Since the currents y_1 and y_2 are obtained with the same electric force X , the number of electrons coming from the filament is the same in each case.

In moving under a uniform electric force through a gas

the electrons do not attain a steady motion until they have traversed a certain distance from the filament. Experiments with photoelectric currents in helium show that the energy of the electrons increases up to a point where about half the electrons from the negative electrode have ionized molecules of the gas. After passing this point there is a slight decrease in the average energy of the electrons in the

Fig. 6.



stream, and the motion approaches a steady state after the stream has traversed a distance b from the electrode where Xb is about 45 or 50 volts when the ratio X/p is about 16 and the gas at 16°C . For distances from the negative electrodes greater than b the currents increase with the distance in accordance with the formula $n_0 e^{ax}$.

In order to estimate the rate at which electrons ionize molecules, when the motion is steady, from the ratio of the

ordinates of the two curves (fig. 6) it is necessary that the potential difference between the filament and the plate B should exceed 45 volts. In order that this condition may be satisfied when the plate is 7 mm. from the filament the value of X should exceed 64 volts per centimetre.

There is also an upper limit to the value of X depending on the potential difference $X \times x$ between the two plates A and B (fig. 1). The curves (fig. 3) show that when the gas is at 10 mm. pressure, the additional process of ionization contributes to the conductivity, when the potential difference $X \times 1.75$ exceeds 125 volts. In order to avoid this effect when the electrons are moving to the upper plate and the distance between the plates is 17.5 millimetres, the electric force should not exceed 70 volts per centimetre.

Hence in the curves (fig. 6), when the electric force is between 64 and 70 volts per centimetre, the difference $(y_2 - y_1)$ of the ordinates corresponding to the same value of X represents the number of molecules ionized by electrons moving through the distance $(x_2 - x_1)$ equal to 3.5 millimetres, when the motion of the electrons is steady. At the points on the curves corresponding to $X = 67$ ($V_{y_1} = 47$ volts) the ratio of the ordinates $y_2/y_1 = 2.0$, which shows that the number of electrons in the stream is exactly doubled in moving through the distance $(x_2 - x_1)$, where $(x_2 - x_1)X = .35 \times 67 = 23.4$ volts.

The gas in these experiments was at 10.6 millimetres pressure, but the average temperature was at least twice the normal in the space traversed by the stream of electrons from the filament to the upper plate. The value of X/p must therefore be taken to be about 14 in these experiments in order to compare the results with those obtained in a gas at 16°C .

The photoelectric currents obtained in helium at about 16°C . (given in Table I.) show that the quantity α does not change to any great extent when X/p varies from 12 to 20, and at these points the photoelectric current is doubled in moving through the distance $(x_2 - x_1)$, where $(x_2 - x_1)X$ is about 23 or 24 volts.

It is evident, therefore, that the action of electrons in ionizing molecules of helium when the gas is traversed by ultra-violet light does not differ appreciably from the action in the absence of ultra-violet light.

LXX. *Some Dynamical Illustrations of the Pressure of Radiation and of Adiabatic Invariance.* By T. H. HAVELOCK; F.R.S.*

Introduction.

1. **T**HE associated ideas of the pressure of vibrations and of certain adiabatic invariants suggest various problems in simple dynamical systems with a moving constraint which are capable of exact solution.

The first one considered is the small transverse vibration of a particle attached to a light string whose tension is assumed constant. One end of the string is fixed; while on the other side of the particle the string passes through a small hole in a plate which is made to move with uniform velocity v . The differential equation of motion can be solved completely in terms of generalized hypergeometric functions; here we require a solution for which the initial position and velocity of the particle have assigned values, and it is more convenient to work out directly an asymptotic expansion for such a solution as v converges to zero. If the plate is moved through any finite distance, we may then calculate the final motion in terms of the initial motion to any required degree of accuracy; in particular, if E is the energy of the motion and n the corresponding frequency, we may examine how the final value of E/n approximates to its initial value when v is made small.

A special case of this problem is obtained by taking the constant length of string on one side of the particle to be infinite, or supposing the particle to move in smooth guides at right angles to the string. Here the complete solution involves more familiar Bessel functions, of which asymptotic expansions are available. This case is essentially the same as the so-called Rayleigh pendulum, and I find that a similar solution of the latter problem has been given recently by Krutkow and Fock †.

Further interest attaches to the similar problems when the vibrating medium is a continuous uniform string. These include the well-known device by which Larmor illustrated the pressure of radiation. By considering incident and reflected simple harmonic waves at a moving reflector, he obtained the pressure of radiation in the form

$$p = \frac{c^2 - v^2}{c^2 + v^2} e_R, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

* Communicated by the Author.

† G. Krutkow and V. Fock, *Zeit. für Phys.* xiii. p. 195 (1923).

where c is the wave velocity, v the velocity of the reflector, and e_R the density of energy in front of the reflector; it should be noted that p and e have in his analysis their average values for simple harmonic waves.

Levi-Civita * refers to the case when the string is of finite length, one end being fixed and the other passing through a moving plate; he remarks that it would not be difficult to determine functions satisfying rigorously the nodal condition both at the fixed end and at the moving reflector. The solution is supplied in the following paper: it was, in fact, this remark which suggested the problems considered here. The solutions examined are those which reduce to simple harmonic vibrations when the velocity of the moving reflector is made infinitesimal; they are used to calculate the pressure on the reflector and also to confirm the adiabatic invariance of E/n in these cases.

Larmor's formula (1) is usually referred to as being valid for a non-dispersive medium in which the average density of energy in a simple harmonic wave is inversely proportional to the square of the wave-length. From this point of view it could be extended to other types of disturbance in such a medium by direct summation †. However, if we remove the restriction that we are dealing with average values of the pressure and of the energy density, it is easy to generalize the result completely from the equations of motion together with the kinematic condition for a travelling node. This is confirmed also by the properties of the general solution when there is a stationary node and a travelling node.

The same arguments apply equally to electromagnetic waves in free space when suitable conditions are chosen for the travelling node.

It is desirable to specify clearly what is meant by the pressure of radiation. Calculations are generally made on the assumption of simple harmonic vibrations and average values are used, the pressure being usually deduced by an application of Lagrange's dynamical equations in generalized coordinates. Here we consider in each case an unlimited medium in which there is a disturbance, which can be analysed into forward and backward waves, such that there is a fixed node and a node travelling away from it with uniform velocity v ; the pressure is defined as the rate of decrease of energy in the region between the two nodes divided by the velocity v .

* T. Levi-Civita, Appendix to Sir Joseph Larmor's lecture on "The Dynamics of Radiation," Inter. Math. Congress, Proc. i. p. 217 (1912).

† Ghosh and Sur, Phys. Rev. xviii. p. 380 (1921).

The actual apparatus for a moving reflector by which this pressure could be realized is of course quite another matter. For a string, a plate with a hole through which the string passes is sufficiently descriptive; but it is no more than that—in fact, the resolved force on the plate due to the tension of the string is not in general equal to the pressure as calculated. One may refer here to some rather artificial devices suggested by Poynting* by which one might imagine this pressure realized in certain cases, such as the motion of a plate through a gas or an elastic solid; incidentally, Poynting refers to the pitfalls which beset the subject, the two chief being the definition of the pressure and the fact that when second-order terms are used for its calculation the original equations may no longer be valid and it may not be permissible to assume simple harmonic motion. In a recent elaborate study by Brillouin† the distinction is carefully drawn between the pressure on an ideal reflector immersed in a continuous medium and the pressure on a reflector which bounds the medium; the conclusion seems to be drawn that most previous writers, with the exception of Lorentz, have failed to observe the distinction.

However, we are not concerned specially with these considerations in what follows; the problems are comparatively simple dynamical cases in which the conditions are specified in the manner indicated, and assuming these conditions certain exact solutions of the equations of motion are investigated.

In a last section some application is made to dispersive media, the example being a uniform string at constant tension in which each particle is attracted to its equilibrium position by a force proportional to displacement. From considerations of energy changes, it appears that the formula (1) for the pressure of radiation holds also in this case, when suitably interpreted. This is also confirmed for the particular case of simple harmonic waves incident upon and reflected by a moving reflector; further, when average values are considered, the connexion with group velocity and flow of energy is shown.

For a fixed reflector it follows that the pressure is equal to the density of energy in front of the reflector. This is in apparent contradiction with the usual statement for a dispersive medium, that the pressure is U/V times the energy density, where V is wave velocity and U is group velocity. The results are harmonized by noticing that in the latter

* J. H. Poynting, *Phil. Mag.* ix. p. 393 (1905).

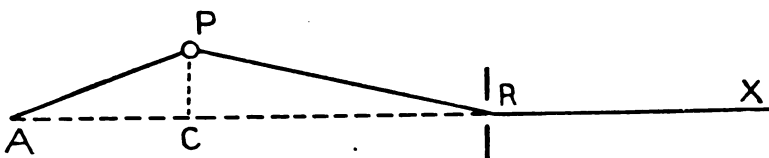
† L. Brillouin, "La Théorie de Solides et les Quanta," *Ann. Ecol. Norm.* xxxvii. (1920).

expression the result only applies to simple harmonic waves and the energy density in question is the average value over the whole range of medium in front of the reflector; the result obtained here is more general, and in it the energy density is that immediately in front of the reflector.

Vibrations of a Particle.

2. A particle P of mass m is attached to a light string APRX stretched at constant tension T ; R is a plate with a small smooth hole through which the string passes.

Fig. 1.



If $AC=a$, and $CR=b+rt$, the equation of motion for small displacement y is, with the usual approximation,

$$(b+rt)\frac{d^2y}{dt^2} + \frac{T}{ma}(a+b+rt)y = 0. \quad (2)$$

If we take the energy at any instant to be

$$E = \frac{1}{2}m\dot{y}^2 + \frac{1}{2}Ty^2\left(\frac{1}{a} + \frac{1}{b+rt}\right), \quad (3)$$

then from the definition already given, the pressure p of the vibrations upon the plate R is

$$p = -\frac{1}{v}\dot{E} = \frac{1}{2}T\frac{\dot{y}^2}{(b+rt)^2}, \quad (4)$$

after using (2). To this order, the value is the same as the resolved force on the plate, namely $T(1-\cos \angle PRC)$. The same result also follows if we use the Lagrange equations with the length CR as a generalized coordinate. No discrepancy arises in this case, since the moving constraint affects one of the parameters of the system without acting directly upon the coordinates of the particle. We shall see later that it is different when we take into account the inertia of the string.

3. We require the solution of (2) when y and $\dot{y}$ have given initial values and in a form suitable for small values of r but with rt finite.

If we put

$$x = (b + vt)/a : \quad k^2 = aT/mr^2, \quad . \quad . \quad . \quad (5)$$

the equation becomes

$$\frac{d^2 y}{dx^2} + k^2 \left(1 + \frac{1}{x}\right) y = 0. \quad . \quad . \quad . \quad (6)$$

The complete solution may be written in various alternative forms ; for instance,

$$y = A W_{-\frac{1}{2}ki, \frac{1}{2}}(2ikx) + B W_{\frac{1}{2}ki, \frac{1}{2}}(-2ikx), \quad . \quad . \quad (7)$$

where A, B are arbitrary constants, and $W_{m,n}$ is a confluent hypergeometric function. However, it is more direct to obtain from the differential equation (6) an asymptotic expansion of the required solution suitable for large values of the parameter k .

We shall use accents to denote differentiation with respect to x ; then if y_0 and $\dot{y}_0$ are the initial values for equation (2), those for equation (6) are

$$y = y_0 : \quad y' = k\dot{y}_0 \sqrt{am/T} ; \quad \text{for } x = b/a = x_0. \quad . \quad (8)$$

Assume a solution of the form

$$y = e^{ik\omega} \left(\phi_0 + \frac{\phi_1}{k} + \frac{\phi_2}{k^2} + \dots \right), \quad . \quad . \quad . \quad (9)$$

where $\omega, \phi_0, \phi_1, \dots$ are functions of x . Substitute in (6) and equate to zero the coefficients of $k^2, k, k^0, k^{-1}, \dots$; we then obtain the series of equations

$$\left. \begin{aligned} \omega'^2 &= 1 + x^{-1}, \\ \omega''\phi_0 + 2\omega'\phi_0' &= 0, \\ i\omega''\phi_1 + 2i\omega'\phi_1' + \phi_0'' &= 0, \\ i\omega''\phi_2 + 2i\omega'\phi_2' + \phi_1'' &= 0, \\ \dots\dots\dots & \end{aligned} \right\} \quad . \quad . \quad . \quad (10)$$

Similarly, if we assume a solution

$$y = e^{-ik\omega} \left(\psi_0 + \frac{\psi_1}{k} + \frac{\psi_2}{k^2} + \dots \right), \quad . \quad . \quad . \quad (11)$$

we obtain a set of equations like (10) with $-i$ instead of $+i$. The equations for ω and the ϕ 's and ψ 's are differential equations of the first order which can be solved for the various functions step by step.

We now take the complete solution to be the sum of (9) and (11), and we have to satisfy the initial conditions (8). For this purpose we take, from the first two equations in (10),

$$\omega = \int_{x_0}^x \sqrt{(1+x^{-1})} \cdot dx, \quad . \quad . \quad . \quad (12)$$

and then the initial conditions give, for $x=x_0$,

$$\left. \begin{aligned} \phi_0 + \psi_0 &= y_0, \\ i\omega' \phi_0 - i\omega' \psi_0 &= \dot{y}_0 \sqrt{(am/T)}, \\ \phi_n + \psi_n &= 0, \\ i\omega' (\phi_n - \psi_n) + \phi'_{n-1} + \psi'_{n-1} &= 0, \end{aligned} \right\} \quad . \quad . \quad (13)$$

for $n=1, 2, 3, \dots$.

These give the following values:

$$\left. \begin{aligned} \phi_0(x_0) &= \frac{1}{2}y_0 - \frac{1}{2}i\dot{y}_0 \sqrt{(am/T)} / \omega'(x_0), \\ \phi_1(x_0) &= \frac{1}{4}i\dot{y}_0 \omega''(x_0) / \{\omega'(x_0)\}^2, \\ \phi_n(x_0) &= 0; \quad n = 2, 3, \dots \end{aligned} \right\} \quad . \quad . \quad (14)$$

with similar values for the ψ 's with the sign of i changed.

We can now integrate completely the subsidiary equations (13), and obtain

$$\begin{aligned} \phi_0 &= \left\{ \frac{1}{2}y_0 - \frac{1}{2}i\dot{y}_0 \frac{\sqrt{(am/T)}}{\omega'(x_0)} \right\} \left\{ \frac{\omega'(x_0)}{\omega'(x)} \right\}^{\frac{1}{2}}, \\ \phi_1 &= \frac{i}{2\{\omega'(x)\}^{\frac{1}{2}}} \int_{x_0}^x \frac{\phi_0''(x)}{\{\omega'(x)\}^{\frac{1}{2}}} dx + \frac{1}{4}i\dot{y}_0 \left\{ \frac{\omega''(x_0)}{\omega'(x)} \right\}^{\frac{1}{2}} \left\{ \frac{\omega'(x_0)}{\omega'(x)} \right\}^{\frac{3}{2}}, \\ \phi_n &= \frac{i}{2\{\omega'(x)\}^{\frac{1}{2}}} \int_{x_0}^x \frac{\phi_{n-1}''(x)}{\{\omega'(x)\}^{\frac{1}{2}}} dx; \quad n = 2, 3, \dots, \quad . \quad . \quad (15) \end{aligned}$$

together with similar equations for the ψ 's.

With these values the series (9) + (11) satisfies formally the conditions of the problem. It remains to be proved that it is the asymptotic expansion, for $k \rightarrow \infty$, of that integral of (6) which is determined by the initial values (8). It is unnecessary to work through the detailed analysis; the method consists in forming, by a suitable chain of approximations, a convergent series for the required solution of (6) and showing that we obtain the previous formal solution by taking the asymptotic expansions of the terms in the convergent series. It may suffice to refer * to the solution of a

* J. Horn, Math. Ann. lii. pp. 271 and 340 (1899).

more general equation by this method, and to state that the formal solution is valid for positive values of x ; consequently, the corresponding solution of (2) is valid for $t > 0$ provided we have $b > 0$.

It will be seen, from (15), that the expressions for the functions ϕ and ψ soon become rather lengthy. Ultimately we shall only require ϕ_0 and ψ_0 , but the next two terms have also been calculated so that we may have the expressions for y and $\dot{y}$ up to terms in k^{-1} ; with the given conditions the series (9) + (11) leads to real series multiplied by $\cos k\omega$ and $\sin k\omega$.

Collecting the various results, we have

$$\begin{aligned}
 y \sim & \left(1 + \frac{1}{x}\right)^{-\frac{1}{2}} \left\{ y_0 \left(1 + \frac{1}{x_0}\right)^{\frac{1}{2}} \cos k\omega \right. \\
 & \quad \left. + \dot{y}_0 \left(\frac{am}{T}\right)^{\frac{1}{2}} \left(1 + \frac{1}{x_0}\right)^{-\frac{1}{2}} \sin k\omega \right\} \\
 & + \frac{1}{k} \left[\frac{1}{8} \dot{y}_0 \left(\frac{am}{T}\right)^{\frac{1}{2}} \left(1 + \frac{1}{x_0}\right)^{-\frac{1}{2}} \left(1 + \frac{1}{x}\right)^{-\frac{1}{2}} \left(\frac{9 + 12x + 8x^2}{6x^{\frac{1}{2}}(1+x)^{\frac{3}{2}}} \right. \right. \\
 & \quad \left. \left. - \frac{9 + 12x_0 + 8x_0^2}{6x_0^{\frac{1}{2}}(1+x_0)^{\frac{3}{2}}} \right) \cos k\omega \right. \\
 & \quad \left. - \left\{ \frac{1}{8} y_0 \left(1 + \frac{1}{x_0}\right)^{\frac{1}{2}} \left(1 + \frac{1}{x}\right)^{-\frac{1}{2}} \left(\frac{9 + 12x + 8x^2}{6x^{\frac{1}{2}}(1+x)^{\frac{3}{2}}} - \frac{9 + 12x_0 + 8x_0^2}{6x_0^{\frac{1}{2}}(1+x_0)^{\frac{3}{2}}} \right) \right. \right. \\
 & \quad \left. \left. + \frac{1}{4} y_0 x_0^{-2} \left(1 + \frac{1}{x_0}\right)^{-\frac{5}{2}} \left(1 + \frac{1}{x}\right)^{-\frac{1}{2}} \right\} \sin k\omega \right] + \dots, \dots \quad (16)
 \end{aligned}$$

where $x = (b + vt)/a$; $x_0 = b/a$; $k^2 = aT/mv^2$; and

$$\begin{aligned}
 \omega = & x^{\frac{1}{2}}(1+x)^{\frac{1}{2}} - x_0^{\frac{1}{2}}(1+x_0)^{\frac{1}{2}} - \log \{ (1+x)^{\frac{1}{2}} - x^{\frac{1}{2}} \} \\
 & + \log \{ (1+x_0)^{\frac{1}{2}} - x_0^{\frac{1}{2}} \}. \quad (17)
 \end{aligned}$$

We may now write down $\dot{y}$ to the same order, but we shall record only the first terms:

$$\begin{aligned}
 \dot{y} \left(\frac{am}{T}\right)^{\frac{1}{2}} \sim & \left(1 + \frac{1}{x}\right)^{\frac{1}{2}} \left\{ \dot{y}_0 \left(\frac{am}{T}\right)^{\frac{1}{2}} \left(1 + \frac{1}{x_0}\right)^{-\frac{1}{2}} \cos k\omega \right. \\
 & \quad \left. - y_0 \left(1 + \frac{1}{x_0}\right)^{\frac{1}{2}} \sin k\omega \right\}. \quad (18)
 \end{aligned}$$

4. After this digression on the solution of the equation, which is perhaps of interest in itself, we may return to the dynamical problem.

Before the time $t=0$ we suppose the plate R to be fixed

and the particle to be making simple harmonic vibrations of frequency n_0 , where

$$n_0 = \left\{ \left(\frac{T}{m} \right) \cdot \left(\frac{1}{a} + \frac{1}{b} \right) \right\}^{\frac{1}{2}}.$$

Then the plate is moved with uniform velocity v for a finite distance until the length $b + vt = c$ and is stopped; after this time the particle vibrates with frequency

$$n = \left\{ \left(\frac{T}{m} \right) \cdot \left(\frac{1}{a} + \frac{1}{c} \right) \right\}^{\frac{1}{2}}.$$

If v is small, so that k is large, the values of y and $\dot{y}$ when the plate is stopped are given by (16) and (18). It seems permissible to neglect any impulsive changes which might be supposed to occur at the starting and stopping of the plate, because of the idealized nature of the apparatus; the string is such that its inertia may be neglected, and further, that its tension is instantaneously adjusted to the constant value T .

With v small, we may take the first terms in (16) and (17), and we have for the energy after the displacement

$$\begin{aligned} E &= \frac{1}{2} m v \dot{y}^2 + \frac{1}{2} T y^2 (a^{-1} + c^{-1}), \\ &\sim \frac{1}{2} \frac{T}{a} \left(1 + \frac{a}{c} \right)^{\frac{1}{2}} \left\{ \dot{y}_0^2 \left(\frac{am}{T} \right) \left(1 + \frac{a}{b} \right)^{-\frac{1}{2}} + y_0^2 \left(1 + \frac{a}{b} \right)^{\frac{1}{2}} \right\}, \\ &\sim \left(\frac{1}{a} + \frac{1}{c} \right)^{\frac{1}{2}} \left(\frac{1}{a} + \frac{1}{b} \right)^{-\frac{1}{2}} E_0. \end{aligned}$$

Hence we have

$$E/n \sim E_0/n_0. \quad . \quad . \quad . \quad . \quad . \quad (19)$$

5. As a particular case of this problem, suppose the particle to move between smooth guides through C at right angles to OR ; for small motions this is analytically similar to the Rayleigh pendulum, a simple pendulum swinging under gravity with the length altering at a uniform rate. The equation of motion, with the same notation as before, is

$$(b + vt) \frac{d^2 y}{dt^2} + \frac{T}{m} y = 0. \quad . \quad . \quad . \quad . \quad (20)$$

The complete solution of this equation is

$$y = x^{\frac{1}{2}} \{ A J_1(2kx^{\frac{1}{2}}) + B N_1(2kx^{\frac{1}{2}}) \}, \quad . \quad (21)$$

where $x = b + vt$; $k^2 = T/mv^2$.

We have also

$$\dot{y} = v y' = k v \{ A J_0(2kx^{\frac{1}{2}}) + B N_0(2kx^{\frac{1}{2}}) \}. \quad (22)$$

Using the formula

$$J_1(x) N_0(x) - J_0(x) N_1(x) = 2/\pi x,$$

we have

$$\begin{aligned} A &= (\pi/v) \{ k v y_0 N_0(2kb^{\frac{1}{2}}) - b^{\frac{1}{2}} \dot{y}_0 N_1(2kb^{\frac{1}{2}}) \}, \\ B &= (\pi/v) \{ b^{\frac{1}{2}} \dot{y}_0 J_1(2kb^{\frac{1}{2}}) - k v y_0 J_0(2kb^{\frac{1}{2}}) \}. \end{aligned} \quad (23)$$

Suppose now that

$$\left. \begin{aligned} y &= C_0 \sin(n_0 t + \alpha_0), & \text{for } t < 0, \\ y &= C \sin(nt + \alpha), & \text{for } t > (c-b)/v, \end{aligned} \right\} \quad (24)$$

while for the intervening time, y is given by (21); in (24) we have $n_0 = kv/b^{\frac{1}{2}}$, $n = kv/c^{\frac{1}{2}}$.

After a little reduction we obtain

$$\begin{aligned} C \sin \{ k(c-b)c^{-\frac{1}{2}} + \alpha \} &= c^{\frac{1}{2}} \{ A J_1(2kc^{\frac{1}{2}}) + B N_1(2kc^{\frac{1}{2}}) \}, \\ C \cos \{ k(c-b)c^{-\frac{1}{2}} + \alpha \} &= c^{\frac{1}{2}} \{ A J_0(2kc^{\frac{1}{2}}) + B N_0(2kc^{\frac{1}{2}}) \}. \end{aligned} \quad (25)$$

With v small so that the transformation is made slowly, we may use the first terms in the asymptotic expansions of the Bessel functions, namely

$$\begin{aligned} \sqrt{\frac{1}{2}\pi u} J_0(u) &\sim \cos(u - \tfrac{1}{4}\pi); & \sqrt{\frac{1}{2}\pi u} N_0(u) &\sim \sin(u - \tfrac{1}{4}\pi); \\ \sqrt{\frac{1}{2}\pi u} J_1(u) &\sim \sin(u - \tfrac{1}{4}\pi); & \sqrt{\frac{1}{2}\pi u} N_1(u) &\sim -\cos(u - \tfrac{1}{4}\pi). \end{aligned}$$

From (23) we find

$$\begin{aligned} A &\sim \sqrt{(\pi k/b^{\frac{1}{2}})} C_0 \cos\left(2kb^{\frac{1}{2}} - \frac{\pi}{4} - \alpha_0\right), \\ B &\sim \sqrt{(\pi k/b^{\frac{1}{2}})} C_0 \sin\left(2kb^{\frac{1}{2}} - \frac{\pi}{4} - \alpha_0\right). \end{aligned} \quad (26)$$

With a similar reduction (25) now gives

$$C \frac{\sin \left\{ \frac{k(c-b)}{c^{\frac{1}{2}}} + \alpha \right\}}{\cos \left\{ \frac{k(c-b)}{c^{\frac{1}{2}}} + \alpha \right\}} \sim \frac{c^{\frac{1}{2}}}{b^{\frac{1}{2}}} C_0 \frac{\sin \left\{ 2k(c^{\frac{1}{2}} - b^{\frac{1}{2}}) + \alpha_0 \right\}}{\cos \left\{ 2k(c^{\frac{1}{2}} - b^{\frac{1}{2}}) + \alpha_0 \right\}}. \quad (27)$$

Thus the change in the amplitude of the vibration by this slow transformation follows the law

$$C/C_0 \sim (c/b)^{\frac{1}{2}}, \quad (28)$$

and since the energy is proportional to the square of the amplitude and inversely proportional to the length of string, the adiabatic invariance of E/μ follows from this result.

Vibration of Uniform String.

6. With T as the tension of the string and ρ the line density, the equation of motion is

$$\frac{\partial^2 y}{\partial t^2} = c^2 \frac{\partial^2 y}{\partial x^2}; \quad c^2 = T/\rho. \quad (29)$$

The density of energy per unit length is given by

$$e = \frac{1}{2}\rho(\partial y/\partial t)^2 + \frac{1}{2}T(\partial y/\partial x)^2. \quad (30)$$

Now suppose that the motion of the infinite string is such that the origin O is a fixed node and the point R given by $x=a+vt$ is a node moving with uniform velocity v . The rate of increase of energy E in the portion OR of the string is

$$\frac{\partial E}{\partial t} = \frac{\partial}{\partial t} \int_0^{a+vt} e \, dx = v e_R + \int_0^{a+vt} \frac{\partial e}{\partial t} \, dx. \quad (31)$$

After a partial integration, using (29) and (30) and the condition $y=0$ at O , this leads to

$$\frac{\partial E}{\partial t} = v e_R + T \left(\dot{y} \frac{\partial y}{\partial x} \right)_R. \quad (32)$$

But the kinematic condition at the travelling node is

$$\dot{y} + v \frac{\partial y}{\partial x} = 0. \quad (33)$$

Hence we have

$$e_R = \frac{1}{2}\rho(c^2 + v^2) \left(\frac{\partial y}{\partial x} \right)_R^2.$$

$$\partial E/\partial t = v e_R - \rho c^2 v \left(\frac{\partial y}{\partial x} \right)_R^2 = \frac{1}{2} v \rho (v^2 - c^2) \left(\frac{\partial y}{\partial x} \right)_R^2.$$

If we think of the travelling node R as produced by an ideal perfect reflector moving with velocity v , the equivalent pressure of the vibrations at R is then

$$p = - \frac{1}{v} \frac{\partial E}{\partial t} = \frac{c^2 - v^2}{c^2 + v^2} e_R. \quad (34)$$

We notice incidentally that if we picture the reflector in this case as a plate with a small hole through which the string passes, the pressure p so calculated is less than the resolved statical tension of the string if we assume the string undisturbed beyond the plate; for the latter force, being $\frac{1}{2}T(\partial y/\partial x)_R^2$, is equal to $c^2 e_R/(c^2 + v^2)$.

The result (34) is Larmor's formula generalized, without

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being confined to simple harmonic waves and average values
of the quantities involved.

7. The general solution of (29) is

$$y = f(ct-x) + F(ct+x), \quad . \quad . \quad . \quad (35)$$

and the boundary conditions are $y=0$ for $x=0$ and for
 $x=a+vt$. Hence the motion is given by

$$y = f(ct-x) - f(ct+x), \quad . \quad . \quad . \quad (36)$$

where f satisfies the functional equation

$$f\{(c-v)t-a\} = f\{(c+v)t+a\}. \quad . \quad . \quad . \quad (37)$$

We have now

$$\begin{aligned} e_R &= \rho c^2 [f''\{(c-v)t-a\} + f''\{(c+v)t+a\}] \\ &= \frac{2\rho c^2(c^2+v^2)}{(c+v)^2} f''\{(c-v)t-a\}, \end{aligned}$$

$$\begin{aligned} \left(\dot{y} \frac{\partial y}{\partial x}\right)_R &= c[f''\{(c-v)t-a\} - f''\{(c+v)t+a\}] \\ &= -\frac{4c^2v}{(c+v)^2} f''\{(c-v)t-a\}. \end{aligned}$$

Substituting in (32), we deduce again the result (34).

8. We may examine some particular solutions of the
functional equation (37). It is of the form

$$f(\alpha u + \beta) = f(u), \quad . \quad . \quad . \quad (38)$$

where $\alpha = (c+v)/(c-v)$ and $\beta = 2ac/(c-v)$.

If we write

$$\left. \begin{aligned} f(u) &= \phi(\xi), & f(\alpha u + \beta) &= \phi(\xi+1), \\ u &= \psi(\xi), & \alpha u + \beta &= \psi(\xi+1), \end{aligned} \right\} \quad . \quad (39)$$

then (38) is replaced by the pair of difference equations

$$\left. \begin{aligned} \phi(\xi+1) - \phi(\xi) &= 0, \\ \psi(\xi+1) - \alpha\psi(\xi) &= \beta. \end{aligned} \right\} \quad . \quad . \quad . \quad (40)$$

Solutions of these are obtained by the ordinary rules for
difference equations; and so we arrive at solutions of (38)
by eliminating ξ from

$$\left. \begin{aligned} f(u) &= \phi(\xi), \\ u = \psi(\xi) &= \frac{\beta}{1-\alpha} + \alpha^\xi \chi(\xi), \end{aligned} \right\} \quad . \quad . \quad (41)$$

where ϕ and χ are arbitrary periodic functions of ξ of unit period. In particular, if we take

$$\phi(\xi) = A \sin 2s\pi\xi, \quad \chi(\xi) = -\beta/(1-\alpha),$$

where s is an integer, we have

$$f(u) = A \sin \left[2s\pi \frac{\log \{1-u(1-\alpha)\beta\}}{\log \alpha} \right]. \quad (42)$$

Returning now to (36), and replacing the values of α and β , we have a motion of the vibrating string such that there is a stationary node O at $x=0$ and a travelling node R at $x=a+vt$, namely

$$y = A \sin 2s\pi \frac{\log \{1+r(ct+x)/ca\}}{\log \{(c+v)/(c-v)\}} \\ - A \sin 2s\pi \frac{\log \{1+r(ct-x)/ca\}}{\log \{(c+v)/(c-v)\}}. \quad (43)$$

It may be easily verified that the limiting value of this expression for $v \rightarrow 0$ is the ordinary case of steady vibrations,

$$y = 2A \sin \frac{s\pi x}{a} \cos \frac{s\pi ct}{a}. \quad (44)$$

The expression (43) may be used to examine the motion of the string between O and R, assuming a and t both positive, for various ratios of v to c .

9. It is unnecessary to repeat the calculation for the pressure of the vibrations at R, as the particular case is included in the general formulæ of § 7.

We shall not attempt to solve the general problem of the finite motion of the reflecting plate R, as was done in § 4 for the simple particle. It would mean starting with R fixed and the string performing some normal vibration; the plate R would then be moved with uniform velocity through a certain distance and stopped. We should have to fit given initial conditions by a general solution, possibly made up of a series of expressions like (43). Further, we should have to consider the possibility of impulsive disturbances at the beginning and end of the motion, which would require a closer specification of the action of the plate; it may be presumed that such disturbances would be narrow pulses emitted from R at a sudden change in velocity. We are concerned chiefly with the results when v is small; and as (43) approximates then to a normal vibration, we shall calculate from it the change

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in the energy as the length of the string increases from
 a to b .

Making use of the general formulæ in § 7, we have

$$E_b - E_a = -\frac{2\rho c^2(c-v)}{c+v} \int_0^{(b-a)/v} [f'\{(c-v)t-a\}]^2 dt, \quad (45)$$

where

$$f(u) = A \sin \left\{ 2s\pi \log \left(1 + \frac{vu}{ca} \right) / \log \frac{c+v}{c-v} \right\}. \quad (46)$$

Putting $a+vt=l$, this gives

$$E_b - E_a = -\frac{8s^2\pi^2 v^2 c^2 \rho}{(c^2-v^2) \left\{ \log \frac{(c+v)l}{(c-v)} \right\}^2} \\ \times \int_a^b \cos^2 \left[2s\pi \frac{\log \{(c-v)l/ca\}}{\log \{(c+v)/(c-v)\}} \right] dl. \quad (47)$$

If θ is the angle under the integral sign, and if α is written
for $\log (c+v)/(c-v)$, the value of the integral is one-half of

$$\frac{1}{\alpha} - \frac{1}{b} + \frac{4s\pi\alpha}{16s^2\pi^2 + \alpha^2} \left\{ \frac{1}{b} \sin 2\theta_b - \frac{1}{a} \sin 2\theta_a \right\} \\ - \frac{\alpha^2}{16s^2\pi^2 + \alpha^2} \left\{ \frac{1}{b} \cos 2\theta_b - \frac{1}{a} \cos 2\theta_a \right\}.$$

Collecting the results, and expanding, we have

$$E_b - E_a = -s^2\pi^2 c^2 \rho \left[\frac{1}{a} - \frac{1}{b} + \frac{v}{2s\pi cb} \sin \left(\frac{2s\pi c}{v} \log \frac{b}{a} \right) + \dots \right]. \quad (48)$$

Thus as $c \rightarrow 0$, we have

$$E_b - E_a \sim -s^2\pi^2 c^2 \rho \left(\frac{1}{a} - \frac{1}{b} \right).$$

But, to the same approximation, we have from (44),
 $E_a = s^2\pi^2 c^2 \rho / u$; thus $bE_b \sim aE_a$.

Since the frequency of a normal vibration is inversely pro-
portional to the length of string, this is the required adiabatic
invariance of E/ν .

Electromagnetic Waves.

10. The preceding analysis can be applied directly to
electrical vibrations in free space. We shall confine our
attention to plane waves with wave fronts perpendicular

to Ox ; if E and H are the electric and magnetic vectors,

$$e = \frac{1}{2}E^2 + \frac{1}{2}H^2,$$

and the equation for flow of energy is

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x}(cEH) = 0. \quad (49)$$

Consider a disturbance for which the point O is a stationary node for E , and the point R a travelling node for $E - vH/c$; so that

$$E = 0 \text{ for } x = 0; \quad E - \frac{v}{c}H = 0 \text{ for } x = a + vt. \quad (50)$$

Then the rate of increase of energy in the region OR is

$$\frac{\partial}{\partial t} \int_0^{a+vt} e dx = ve_R - c(EH)_R = -\frac{1}{2}v \left(1 - \frac{v^2}{c^2}\right) H_R^2, \quad (51)$$

since

$$e_R = \frac{1}{2}v \left(1 + \frac{v^2}{c^2}\right) H_R^2. \quad (52)$$

Hence, if this nodal condition is the boundary condition for an ideal perfect reflector in motion, the corresponding pressure of the vibrations is $(c^2 - v^2)e_R/(c^2 + v^2)$; this, of course, agrees with the usual calculation from electrodynamic theory for the mechanical force on the reflector.

If we have a fixed perfect conductor at the plane $x=0$ and a moving perfect conductor at $x=a+vt$, then plane disturbances in the region between them are given by

$$\begin{aligned} E &= f'(ct-x) - f'(ct+x), \\ H &= f'(ct-x) + f'(ct+x), \end{aligned} \quad (53)$$

where f' satisfies the functional equation

$$(c-v)f'\{(c-v)t-a\} = (c+v)f'\{(c+v)t+a\}.$$

These satisfy the equations and the conditions (50). Referring back to equations (38)-(42), particular types of solution can be written down; for instance, we may take, in (53),

$$f'(u) = \frac{1}{ca+vu} \sin \left[2\pi \frac{\log(1+vu/ca)}{\log(c+v)/\log(c-v)} \right]. \quad (54)$$

With the help of these solutions one might study in detail the problems of the previous sections; for instance, the change produced in a steady normal vibration between two fixed planes if one of the planes is moved with uniform velocity through a finite distance and then stopped.

Dispersive Medium and Group Velocity.

11. As a simple case of a dispersive medium we consider the transverse vibrations of a uniform string, at constant tension T , each particle of which is attracted to its equilibrium position by a force proportional to displacement*.

The equation of motion is of the form

$$\frac{\partial^2 y}{\partial t^2} - c^2 \frac{\partial^2 y}{\partial x^2} + n^2 y = 0, \quad . \quad . \quad . \quad (55)$$

with $c^2 = T/\rho$; the energy density is

$$e = \frac{1}{2}\rho(\dot{y}^2 + c^2 y'^2 + n^2 y^2); \quad . \quad . \quad . \quad (56)$$

while the flow of energy is given by

$$\frac{\partial e}{\partial t} - \frac{\partial}{\partial x} \left(T \dot{y} \frac{\partial y}{\partial x} \right) = 0. \quad . \quad . \quad . \quad (57)$$

If there is a stationary node at O , and a travelling node at R , so that

$$\dot{y} + v y' = 0, \text{ for } x = a + vt,$$

then by the same process as before, from the rate of decrease of energy in OR , we find

$$p = \frac{1}{2}\rho(c^2 - v^2) \left(\frac{\partial y}{\partial x} \right)_R^2 = \frac{c^2 - v^2}{c^2 + v^2} e_R. \quad . \quad . \quad (58)$$

It appears that Larmor's expression has a still wider application in that it may include dispersive media. We may verify this conclusion for simple harmonic waves.

Suppose there are forward and backward waves of equal amplitude and adjusted so that there is a node R travelling with velocity v ; there is now no stationary node.

We have

$$y = \sin \kappa_1(V_1 t - x) - \sin \kappa_2(V_2 t + x), \quad . \quad . \quad (59)$$

where the wave velocity V is given by

$$\kappa V = \sqrt{(\kappa^2 c^2 + n^2)}. \quad . \quad . \quad . \quad (60)$$

If we take the travelling node to be at $x = vt$, we have

$$(\kappa_2^2 c^2 + n^2)^{\frac{1}{2}} + \kappa_2 v = (\kappa_1^2 c^2 + n^2)^{\frac{1}{2}} - \kappa_1 v. \quad . \quad . \quad (61)$$

Thus the wave-length of the reflected wave is found from

$$\kappa_2 = \frac{\kappa_1(c^2 + v^2) - 2v(\kappa_1^2 c^2 + n^2)^{\frac{1}{2}}}{c^2 - v^2}. \quad . \quad . \quad (62)$$

*"The Propagation of Disturbances in Dispersive Media," Camb. Tracts, No. 17, p. 58 (1914).

There is no fixed node ; but we may consider the rate of increase of energy between the fixed point O and the moving point R. It is

$$\frac{\partial}{\partial t} \int_0^{rt} e dx = e_R + T \left(\dot{y} \frac{\partial y}{\partial x} \right)_R - T \left(\dot{y} \frac{\partial y}{\partial x} \right)_0. \quad (63)$$

The last term represents the rate of work of the tension at O upon the medium outside the range OR ; and therefore, as before, we consider the equivalent pressure of radiation at R to be given by

$$-p = e_R + \frac{T}{v} \left(\dot{y} \frac{\partial y}{\partial x} \right)_R. \quad (64)$$

From (56), (59), and (62), if we write

$$\kappa_2(V_2 - v)t = \kappa_1(V_1 + v)t = \alpha, \quad (65)$$

we obtain

$$\begin{aligned} e_R &= \frac{1}{2} \rho (c^2 + v^2) (\kappa_1 + \kappa_2)^2 \cos^2 \alpha \\ &= 2\rho \frac{c^2 + v^2}{(c - v)^2} \{ \kappa_1 c^2 - v(\kappa_1^2 c^2 + n^2)^{\frac{1}{2}} \}^2 \cos^2 \alpha, \end{aligned} \quad (66)$$

$$\left(\dot{y} \frac{\partial y}{\partial x} \right)_R = - \frac{4v}{(c^2 - v^2)^2} \{ \kappa_1 c^2 - v(\kappa_1^2 c^2 + n^2)^{\frac{1}{2}} \}^2 \cos^2 \alpha. \quad (67)$$

Hence the equivalent pressure is

$$p = \frac{2\rho}{c^2 - v^2} \{ \kappa_1 c^2 - v(\kappa_1^2 c^2 + n^2)^{\frac{1}{2}} \}^2 \cos^2 \alpha = \frac{c^2 - v^2}{c^2 + v^2} e_R. \quad (68)$$

It will be noticed that the pressure is proportional to $(U_1 - v)^2$, where U_1 is the group velocity of the incident wave ; for

$$U = \frac{d(\kappa V)}{d\kappa} = \frac{\kappa c^2}{(\kappa^2 c^2 + n^2)^{\frac{1}{2}}}. \quad (69)$$

But the connexion with group velocity is more direct when we consider the streams of energy in the incident and reflected waves. It must be remembered that in such a treatment we are dealing with average values ; for instance, group velocity for a simple harmonic train is the average rate of flow of energy. Larmor's method of obtaining his formula for the uniform non-dispersive string was to consider the rate of increase of energy as due on the average to the streams of energy through the travelling node ; thus it

Phil. Mag. S. 6. Vol. 47. No. 280. April 1924. 3 D

was given by $e_2(c+v) - e_1(c-v)$, with e_1 and e_2 as the average energy densities in the two wave-trains.

In the present dispersive case, we should have by a similar argument for average values

$$\bar{p} = -\frac{1}{v} \{e_2(U_2+v) - e_1(U_1-v)\} \dots (70)$$

But we have

$$\bar{e} = \frac{1}{2} \rho (\kappa^2 c^2 + n^2) \dots (71)$$

From (62), (69), (70), and (71) after a little reduction, we get

$$\bar{p} = \frac{\rho}{c^2 - n^2} \{ \kappa_1 c^2 - v(\kappa_1^2 c^2 + n^2) \}^2, \dots (72)$$

which is just the average value of the previous expression (68).

In the same way we may remove an apparent discrepancy. It follows from (68) with $v=0$ that $p=e_R$; that is, the pressure of radiation on a stationary reflector is equal to the energy density in front of the reflector. On the other hand, the usual statement, originally made by Rayleigh* and since elaborated by others, is that for a dispersive medium

$$p = \frac{U}{V} e \dots (73)$$

From the introduction of group velocity it is obvious that in (73) we are dealing only with simple harmonic waves and with average values; in fact, e is not the energy density immediately in front of the reflector, but is the average density for simple waves over the whole range of the medium in front of the reflector. Now for a reflector at rest, the reflected wave has the same wave-length as the incident, so from (71)

$$\bar{e} = \rho (\kappa^2 c^2 + n^2), \dots (74)$$

where the average is with respect to time and position.

Further, immediately in front of the reflector, for $v=0$, from (66)

$$e_R = \rho \kappa^2 c^2, \dots (75)$$

where the average with respect to time is taken.

* Rayleigh, Phil. Mag. 1902, or 'Scientific Papers,' v. p. 47.

Since from (60) and (69)

$$U/V = \kappa^2 v^2 / (\kappa^2 c^2 + n^2),$$

it follows that (73) is consistent with (68) for $v=0$. It is, however, only a particular case, for average values; the more general statement is that the pressure is equal to the energy density immediately in front of the stationary reflector.

Whether these results are peculiar to the special medium studied here must be left for further investigation, as well as some interesting questions which arise when the velocity of the reflector is greater than the group velocity of the incident waves or even greater than the velocity of the front of a limited disturbance.

Summary.

The paper contains a study of the solution of the following type of problem, with various applications: the small transverse vibrations of a string stretched at constant tension, one end being fixed and the other passing through a small hole in a plate which moves along the string with uniform velocity v .

1. With a single particle attached to a light string, the equation of motion is solved and an asymptotic expansion found when v is small; this is applied to the adiabatic invariance of E/n , where E is energy and n frequency. A particular case corresponds to the Rayleigh pendulum.

2. With a uniform string, solutions are found which give a stationary node and a travelling node, and similar applications are made.

The pressure of radiation at a moving reflector is examined and the formula $p = (c^2 - v^2)e / (c^2 + v^2)$ is generalized.

3. Similar solutions are indicated for plane electromagnetic waves between fixed and moving planes which are perfect reflectors.

4. When the string is endowed with a certain dispersive property, the pressure of radiation is found to obey the same general formula, and the relation of this to the usual formulae involving group velocity is shown.

LXXI. *The Relation between the Refractivities and the Sizes of the Atoms of Certain Elements.* By J. E. CALTHROP, B.A. (Cantab.), B.Sc. (Lond.) *.

I. *Introduction.*

THE relation between the refractivities and the atomic weights of certain elements has been investigated by Cuthbertson †, who found that the values of $(\mu_D - 1) \times 10^6$, where μ_D is the refractive index for sodium light, were for the elements of a vertical column of the Periodic Table proportional to integers.

For example, in the case of the inert gases the following results were obtained :—

Element.	$(\mu_D - 1) \times 10^6$.	Ratio.
He	34.9	1
Ne	68.7	2
Ar	283.7	8
Kr	427.3	12
Xe	702.0	20

The same ratios were approximately obtained for Groups V., VI., and VII., although in certain cases the discrepancy from this whole number relation was as much as 8–17 per cent.

$(\mu_D - 1) \times 10^6$ was seen to increase with atomic weight in any vertical column, and to decrease with atomic weight in a horizontal row.

Le Bas ‡ has also investigated the regularities of these elements, and has given tables of combined atomic refractivities and of atomic volumes, but the atomic volumes given do not agree with those of Stefan Meyer §. In some cases mean values were given, as the atomic volume depends on the condition of the substance.

The following is the table of atomic volumes as given by Le Bas :—

C.	N.	O.	F.
14.8	12.0	7.4	6.5
Si.	P.	S.	Cl.
30.0	27.0	23.5	21.6
			Br.
			29.0
			I.
			37.0

* Communicated by Prof. C. H. Lees, D.Sc., F.R.S.

† Science Progress, No. 10, iii, p. 283 (Oct. 1908).

‡ 'Nature,' cviii, p. 272 (Oct. 1921).

§ Sommerfeld, 'Atomic Structure,' 1922.

For I, N, and S, mean values were taken.

The following was his table of combined atomic refractivities, where the formula for refractivity was of the Lorentz form :— $\frac{\mu_D^2 - 1}{\mu_D^2 + 2} \cdot \frac{A}{\rho}$, where A is the atomic weight and ρ the density :—

C.	N.	O.	F.
3.36	2.38	1.48	0.67
Si.	P.	S.	Cl.
8.80	7.76	6.79	5.96
	As.	Se.	Br.
	10.50	9.89	8.79
		I.	13.87

From these data Le Bas found differences in the atomic refractivities which correspond to differences in the atomic volumes. Plotting atomic refractivities against atomic volumes he found an approximately linear relation.

He therefore concluded that the atomic refractivities were proportional to the atomic volumes, and also stated that the former were roughly proportional to the valencies in any horizontal row of the Periodic Table. Little mention was made of the inert gases as fitting into this scheme, because of course the combining values of the atomic refractivities are derived from compounds.

II. *Relation between Refractivity and Atomic Size.*

The aim of the present paper is to show that there is an intimate connexion between the refractivities and atomic sizes of a number of gases and vapours. The atomic sizes or volumes are calculated from the results of Prof. W. L. Bragg*, and the term size is employed so that there is no confusion with the usual meaning of atomic volume as employed by Meyer.

Professor Bragg gave a comprehensive list of atomic diameters, and when these are plotted against the atomic numbers, curves showing periodicity similar to those of Meyer's are obtained. In the 4th edition of their 'X-rays and Crystal Structure' the authors, W. H. & W. L. Bragg, prefer the term "combination radius" and emphasize the limitations of the meaning of "atomic diameter." The diameters of the atoms of the inert gases could not, of course, be measured from experiments on crystal structure,

* W. L. Bragg, *Phil. Mag.* xl. p. 169 (1920).

but could be inferred from the positions of these elements in the table. As no value for phosphorus was given, this has been estimated as 1.03 Å for the purposes of the present paper. It cannot be very different from those of sulphur, chlorine, and argon in the same row of the Periodic Table. We therefore take the mean of S 1.02 Å, Cl 1.05 Å, and Ar 1.025 Å, and use 1.03 Å for phosphorus. All the other values used in the following tables are those given in Prof. Bragg's paper.

The refractivities are those from which Cuthbertson derived his simple ratios, and they may be found in his original paper.

III. Data and Results.

The elements examined fall in the following part of the Periodic Table:—

No. of row.	Groups I., II., III., IV.	V.	VI.	VII.	VIII.	O.
1	1 H	...	...	...	...	2 He
2	...	7 N	8 O	9 F	...	10 Ne
3	...	15 P	16 S	17 Cl	...	18 Ar
4	{ a. ... b. ...	...	...	...	...	...
		33 As	34 Se	35 Br	...	36 Kr
5	{ a. ... b. ...	...	...	...	...	...
		...	52 Te	53 I	...	54 Xe

The various quantities are set out in the following tables. The atomic radius is in Ångström units, 10^{-10} metre, the volume in cubic Ångström units, and μ_D refers to sodium light:—

Element.	At. radius r .	$\frac{4}{3} \pi r^3$.	$(\mu_D - 1) \times 10^6$.	ref./vol.
Ne	0.650 Å	1.150	68.7	59.71
Ar	1.025 „	4.512	283.7	62.87
Kr	1.175 „	6.800	427.3	62.83
Xe	1.350 „	10.310	702.0	68.11
Mean.....				63.38

Results for Column VII.

Element.	At. radius r .	$\frac{4}{3} \pi r^3$.	$(\mu_D - 1) \times 10^6$.	ref./vol.
F.....	0.67 Å	1.261	195.0	154.6
Cl	1.05 „	4.852	768.0	158.3
Br	1.19 „	7.060	1125.0	159.3
I	1.40	11.50	1920(v)-2050(v)*	167.0-214.4
Mean of first 3...				157.4

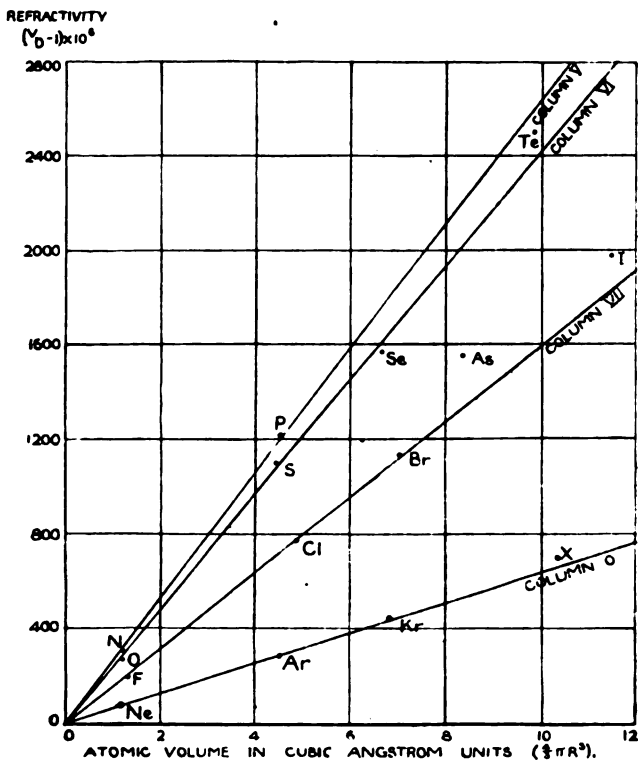
* Results of Hurion for violet and red light.

Results for Column VI.

Element.	At. radius r .	$\frac{4}{3}\pi r^3$.	$(\mu_D - 1) \times 10^6$.	ref./vol.
O.....	0.65 Å	1.152	270.2	234.5
S.....	1.02 „	4.445	1101.0	247.6
Se.....	1.17 „	6.711	1565.0	233.2
Te.....	1.33 „	9.860	2495.0	253.0
Mean.....				242.1

Results for Column V.

Element.	At. radius r .	$\frac{4}{3}\pi r^3$.	$(\mu_D - 1) \times 10^6$.	ref./vol.
N.....	0.65 Å	1.152	297.1	257.9
P.....	1.03 „	4.577	1212.0	264.8
As.....	1.26 „	8.383	1552.0	185.1
Mean of first 2...				261.4



It will be seen that in most cases the ratio of refractivity to the volume is constant in any vertical column, with considerable accuracy.

Arsenic does not seem to fit in the scheme at all well. In the diagram the refractivities and atomic sizes (volumes) are plotted, and give straight lines with slight discrepancies for xenon, iodine, and tellurium. In spite of these it is reasonable to conclude that the refractivities of the elements in a vertical column of the Periodic Table are proportional to the atomic volumes, but that the constant of proportionality is different from column to column.

It is interesting to see how the ratios of the atomic volumes accord with the simple whole number of Cuthbertson and with the actual ratio of the refractivities.

In the following tables we therefore take the first member as 2, and express the others on this basis :—

Column 0.

Element.	Ratio of volumes.	Ratio of refractivities.	Cuthbertson's number.
Ne	2	2	2
Ar	7.85	8.26	8
Kr	11.82	12.44	12
Xe	17.93	20.43	20

Column VII.

F	2	2	2
Cl	7.70	7.88	8
Br	11.12	11.54	12
I	18.24	19.69-21.03	20

Column VI.

O	2	2	2
S	7.72	8.15	8
Se	11.65	11.58	12
Te	17.12	18.47	20

Column V.

N	2	2	2
P	7.94	8.16	8
As	14.56	10.15	12

There is very fair agreement between the ratios of the volumes and the ratios of the refractivities of the first

three members of a column, but the agreement for xenon, iodine, tellurium, and arsenic is not so good. A possible explanation of an approximately whole number relation such as the one suggested by Cuthbertson, is that the atomic radii of elements towards the end of a period tend to a minimum and have approximately the same value. There remains the difficulty, however, that the ratios ref./vol. are not the same for all columns.

IV. Suggested Explanation of Discrepancies.

A small error in the radius produces a much larger error in the volume. Thus an increase of only 4 per cent. in the radius of xenon and iodine and of 1·2 per cent. in that of tellurium would give excellent agreement with the numbers derived from the refractivities of these elements. Bragg's values are for crystals, and it is possible that in the state of gas or vapour the radii are slightly larger than the values occurring in crystals. Thus, for example, Schwendenwein *, employing the dynamic model of A. Landé, finds a radius for iodine of 1·432 Å, which is larger than Bragg's value by about the amount demanded.

This value gives a volume of 12·30 cubic Ångström units, a value for ^{refractivity} of 159·7–166·7 (instead of 157·4 for ^{volume} the other elements of the column), and a value corresponding to Cuthbertson's 20 of 19·51.

Other methods of determining atomic diameters such as those of Rankine from viscosity measurements, of Richards from compressibilities, and of Landé's work on atomic structure give larger values than those given by Bragg, but the ratios for a column are much the same, as the following table, in which Cl is taken as unity, shows:—

Element.	Rankine, viscosity.	Richards, compressibility.	Landé, at. structure.	Davy, X-rays.	Bragg, crystal.
Cl.....	1·0	1·0	1·0	1·0	1·0
Br ...	1·11	1·07	1·12	1·11	1·13
I	1·22	1·21	1·25	1·27	1·33

Thus estimates of the ratios of the radii by various observers differ by as much as 5 per cent. in some cases—that is, by something of the order of the discrepancies found in the present paper.

* Quoted by Grimm, *Zeit's. f. Phys. Chem.* xciii. p. 372 (Oct. 1921).

V. *Values of the Constants for Columns.*

The constants expressing the quotients of the refractivities by the volumes for the various columns of the Periodic Table may be conveniently summarized by the use of a formula due to Mosotti*. Treating the atoms of a gas as perfectly conducting spheres, Mosotti found that:—

$$K - 1 = \frac{1}{2}\pi N^2\sigma^3,$$

where K is the dielectric capacity, N is the number of atoms per c.c., and σ is the diameter of an atom.

This leads to a formula for the refractivity given by $\mu - 1 = \frac{\pi}{4} N\sigma^3 = 0.79N\sigma^3$.

If, therefore, a formula $\mu - 1 = KN\sigma^3$, where K is a constant for a given column, be employed, K is found to have the following values if N be taken as 2.705×10^{19}

Group.....	V.	VI.	VII.	O.
	5.07	4.68	3.04	1.23

The atoms of the inert gases provide the nearest approach to the Mosotti relation, and presumably to perfectly conducting spheres.

So far no simple law has been found for these numbers. Le Bas concluded that for the elements of a row the combined atomic refractivities were roughly proportional to the corresponding valencies. No such rule appears to hold for the numbers found, and it would be useful and interesting if these could be explained.

Abstract.

The refractivities of fifteen elements for sodium light have been plotted against the corresponding atomic volumes, calculated from the estimates of atomic diameters given by Prof. W. L. Bragg from his work on crystal structure. The elements of a vertical column of the Periodic Table when plotted on a graph fall upon a straight line, showing that the refractivity is proportional to the atomic volume, but the ratio $\frac{\text{refractivity}}{\text{volume}}$ decreases from left to right, *i. e.* in the direction of the decreasing valency. That the refractivities of the elements in the last four columns bear approximately

* Jeans's 'Electricity and Magnetism,' 4th ed. p. 130.

the same ratio to one another as noticed by Cuthbertson may possibly be explained by the fact that the atomic radii towards the end of a period have approximately the same value. The different constants obtained for ^{refractivity} _{volume} for the various columns remain to be explained.

East London College,
Feb. 1924.

LXXII. *On a Supposed Limitation of the Second Law of Thermodynamics.*

To the Editors of the Philosophical Magazine.

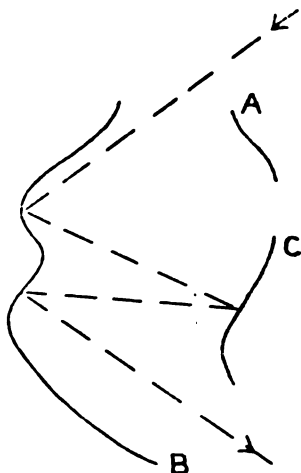
GENTLEMEN,—

IN the January number of the Phil. Mag. for this year (p. 152) Witmer shows by a detailed analysis the fallacy existing in Fairbourn's proof of a limitation of the Second Law of Thermodynamics*. The idea was that vessels of certain shapes immersed in a gas, where the mean free path is large in comparison with the dimensions of the vessel, might cause a motion of the gas to take place in one preponderating direction. Witmer shows that this would not occur for the vessels dealt with by Fairbourn by working out in detail the paths of the reflected gas molecules. It seems worth while, however, to point out that the same may be proved generally for a vessel of any shape whatever by means of the following simple considerations.

Suppose we are dealing with a vessel of arbitrary shape and containing an arbitrary number of apertures A, B, C, etc. In the steady state the number of molecules entering the vessel in a given time must, on the average, be the same as the number leaving during the same period. This must be true whether the vessel creates a general stream of gas in one direction or not. A necessary consequence of this is that any gas molecule which enters the vessel from outside must emerge through one of the apertures after a finite number of collisions with the walls of the vessel; moreover, any path leading from A to B will be reversible and will serve to conduct molecules from B to A. We shall suppose the walls of the vessel to be smooth but otherwise of arbitrary curvature. Any element dS of the interior surface may therefore be considered as plane when its magnitude is decreased indefinitely. If now molecules contained within an elementary convergent or divergent bundle bounded by

* Phil. Mag. (6) xliii. p. 1047 (1922).

the solid angle $d\Omega$ be incident on dS then, after reflexion, these molecules will be contained within an elementary bundle bounded by the same solid angle $d\Omega$; for, if θ be the angle between the normal to dS and the direction of incidence of the bundle, we should have $d\Omega = \sin \theta d\theta d\phi$, where ϕ denotes the azimuth. After reflexion the element of solid angle would be $d\Omega' = \sin \theta' d\theta' d\phi' = d\Omega$, since, by



the laws of reflexion, $\theta = \theta'$, $\phi = \phi'$. The angular aperture therefore of such an elementary bundle will not be altered by reflexion. This will hold for any elementary bundle of molecules crossing an element of cross-section dS of an aperture A and entering the vessel. Such a bundle emerging after a finite number of collisions from some other aperture, B say, will be bounded by the same solid angle. If the directions of motion of molecules outside the vessel are uniformly distributed in all directions, then the number of molecules the directions of motion of which are contained in a beam of given solid angle will be proportional to that solid angle, and one direction of motion will be just as probable as the opposite one.

It follows from this that no resultant motion of the gas molecules will occur in any of these elementary bundles, since the number of molecules entering the beam at B and moving to A will be the same, in any given time, as the number entering at A and moving to B. We may divide up each aperture into elements of cross-section, and the above considerations will apply to every bundle passing through one of these elements of area. It follows, therefore, that if the directions of the gas molecules outside any vessel are

distributed uniformly in all directions, then the same will hold in the steady state for any region in the interior of the vessel, since none of the bundles passing through an element of volume at the point under consideration will contribute anything to the motion of the gas as a whole. The above argument may easily be extended to the case where singularities occur in the surface such as sharp edges or points, and so the result is perfectly general.

In conclusion I wish to thank Prof. Richardson for kindly reading this note over before publication.

Physics Laboratory,
King's College, London.

J. W. FISHER.

LXXIII. *Notices respecting New Books.*

The Theory of Relativity: Three Lectures for Chemists. By ERWIN FREUNDLICH, Director of the Einstein Tower. Translated by H. L. BROSE, with an Introduction by Viscount HALDANE. (Pp. xii + 98.) (London: Methuen & Co., 1924. Price 5s. net.)

The Foundations of Einstein's Theory of Gravitation. By ERWIN FREUNDLICH. Translated by H. L. BROSE, with a Preface by ALBERT EINSTEIN and an Introduction by H. H. TURNER. (Pp. xvi + 140.) (London: Methuen & Co., 1924. Price 6s. net.)

IN the preface to the second of these volumes, Prof. Einstein states that "the author has succeeded in rendering the fundamental ideas of the theory accessible to all who are to some extent conversant with the methods of reasoning of the exact sciences. The relations of the problem to mathematics, to the theory of knowledge, physics and astronomy are expounded in a fascinating style, and the depth of thought of Riemann, a mathematician so far in advance of his time, has in particular received warm appreciation." This is as complete and accurate a summary of the volume as it is possible to give in a brief compass. The English translation was first published in 1919 by the Cambridge University Press. The new edition is translated from the revised and enlarged German edition and contains, in addition, a number of notes by the author containing references to original literature and amplifying various points in the argument. Notes by the translator, entitled "On the Theory of Relativity" and "Some Aspects of Relativity: the Third Test" are also included.

The other volume under review covers somewhat similar ground, in briefer fashion, and omitting practically the whole account of the work of Riemann. It consists of three lectures delivered to a German Chemical Society, though the name of the Society and the dates of delivery are nowhere stated.

In both volumes special stress is laid on the fundamental importance for the generalized theory of the equality of inertial and gravitational mass. In many elementary expositions of the

theory, sufficient prominence is not given to this remarkable relationship.

Both volumes can be confidently recommended as providing brief, accurate and clearly expressed accounts of the ideas at the basis of relativity. The translations are in general good, though in the first volume, p. 35, "constellation" is employed in an unusual manner and it does not conduce to clarity to refer to the two components of a double star as the "star" and the "central body." On p. 37, "the relative motion of the telescope to the star" should read "... to the light from the star."

The Theory of Determinants in the Historical Order of Development. Vol. IV. *The Period 1880 to 1900.* By Sir THOMAS MUIR, D.Sc., LL.D., F.R.S., C.M.G., formerly Superintendent-General of Education in Cape Colony. (Pp. xxxi+508.) (London: Macmillan & Co., 1923. Price 40s. net.)

THIS volume completes Sir Thomas Muir's monumental account of the historical development of the theory of determinants up to the year 1900. The first volume appeared as long ago as 1905 and the concluding volume has been passed through the press since the author's retirement. He is to be congratulated upon the successful completion of the task upon which he embarked many years ago. It originated in his discovery, when engaged upon his 'Treatise on the Theory of Determinants,' that much inaccurate statement prevailed in regard to the authorship and history of various theorems dealing with determinants. He therefore resolved to set about collecting the titles of all the writings which had appeared on the theory up to the end of 1880. This date was later extended to 1900.

The concluding volume follows the same general plan as the preceding volumes which have been reviewed in these pages, a plan which is well known to students of the subject. For purposes of reference the work is unique and as such it demands a place on the shelves of every scientific library. It is complete, as far as the author's extensive investigations can make it, in the sense that no paper which has contributed anything new to the theory is excluded. To each paper, the author has added an illuminating commentary. The mathematician can take up any one of these four volumes and open it at any page, and is sure to find something to interest him.

The completion of Sir Thomas Muir's work has long been looked forward to. The advances of nearly a quarter of a century since 1900 are, however, not dealt with in these volumes. Is it too much to hope that some other enthusiastic student of the subject will take up the task where Sir Thomas Muir has left it?

Relativity and Gravitation. By T. PERCY NUNN, M.A., D.Sc., Professor of Education in the University of London. (Pp. 167 with 10 figures.) (London: University of London Press, 1923. Price 6s. net.)

THIS work is intended to fill a gap between those books dealing with the Theory of Relativity which treat it from the popular

aspect and demand little or no mathematical equipment on the part of the reader and the advanced works which presuppose a somewhat extensive knowledge of mathematics. The standard of mathematical knowledge demanded of the reader is that of the B.Sc. pass degree and, wherever necessary, the mathematical demonstrations are given with sufficient detail for such a reader to pass without difficulty from step to step. The greatest difficulty which this class of reader is likely to find is in the assimilation of the basic ideas of the tensor calculus and, this subject not having been included in his course of studies, he finds its manipulation somewhat difficult. The author has therefore eased the way by establishing the "three crucial phenomena" without employing the tensor calculus. The method consists in determining the coefficients in the expression for ds^2 by consideration of their Galilean values, their values at infinity, and the value of the gravitational potential. Thus the phenomena which have attracted the interest of the 'educated world' are discussed in an easy way, the tensor calculus being developed subsequently.

We are of the opinion that the author has achieved his purpose with considerable success. For the person with little mathematical training or for those whose mathematics are rusty from long disuse, we cannot recommend any volume as more suitable for explaining the foundations of the theory and the principal results which follow from it.

LXXIV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 624.]

February 27th, 1924.--Prof. W. W. Watts, Sc.D., F.R.S.,
Vice-President, in the Chair

THE following communication was read:—

'Age and Origin of the Lough Neagh Clays.' By William Bourke Wright, B.A., F.G.S.

The problem of the age and origin of the Lough Neagh Clays is of old standing. They have, by most geologists, been doubtfully referred to the Pliocene. Lack of exposure and the apparent absence of fossils precluded any exact determination of age. In 1918 a deep bore penetrated them from top to bottom, and smoothed out nearly all difficulties. Careful examination of the cores has enabled the author to draw the following conclusions:—

- (1) The series has a thickness of over 1000 feet, and is subdivisible into:—
 - (a) Upper Clays and Sands.
 - (b) Middle Shales.
 - (c) Lower Clays and Sands.
- (2) The age is Older Tertiary, not Pliocene. This is established by the presence of *Sequoia cuttsiae* Heer and three species of *Dewalquea*.

- (3) The series has suffered about the same amount of folding and faulting as the basaltic lavas upon which it rests.
- (4) A prolonged period of weathering separated the last outpouring of lava and the deposition of the clays.
- (5) The result of this weathering has been the production of about 70 feet of lithomarge, which, being widely distributed over the catchment-areas of the tributary rivers, supplied the kaolin for the formation of the clays.
- (6) The presence of abundant quartz-sand shows that the river-basins extended beyond the basaltic area.
- (7) The Upper Basalt Lavas of Antrim and the underlying Interbasaltic Zone of Weathering, with its contained rhyolitic lavas, are preserved at least locally beneath the Lough Neagh Beds.

A mechanism can be suggested to account for the relatively iron-free nature of the sediments. As it is clear that the clays have been largely derived from the denudation of lithomarge, it is thought that the composition of the latter affords a clue. Lithomarge is largely a mixture of crystalline kaolin with colloidal iron and some bauxite; and it is regarded as probable that the iron, on account of its fine state of subdivision, remained in suspension in the lake, and was carried off over the outlet, while the coarser kaolin was deposited.

LXXV. *Intelligence and Miscellaneous Articles.*

INTERNATIONAL CONFERENCE ON APPLIED MECHANICS.

AN International Conference on Applied Mechanics will be held at Delft, Holland, on April 22nd to 26th. Two of these days will be assigned to sessions in which original communications will be read in the following sections:—(i.) Rational Mechanics; (ii.) The Theory of Elasticity; (iii.) Hydro- and Aero-dynamics (including Aeronautics). Two other days will be devoted to General Meetings for reviewing and discussing the following subjects:—(1) Graphical and numerical methods of solving differential equations; (2) Experimental methods of solving stress problems; (3) Stress problems in plastic media; (4) The theory of rupture; (5) The physical aspects of non-elastic deformations; (6) Friction and lubrication; (7) Motions in rotating fluids; (8) Stability of fluid motions; (9) Wave-motion; (10) The motion of a fluid in the boundary layer along the surface of solids; (11) The turbulence in the oceans and in the atmosphere; (12) The dynamics of the atmosphere.

Intending visitors are requested to communicate with one of the following members of the Executive Committee:—

Prof. C. B. BIEZENO,
Prof. J. M. BURGERS,
Prof. J. A. SCHOUTEN, }

Laboratorium voor Aero- en Hydrodynamica
des Technische Hoogeschool,
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LXXVI. *The Quantum Theory of Radiation.*
By N. BOHR, H. A. KRAMERS, and J. C. SLATER*.

Introduction.

IN the attempts to give a theoretical interpretation of the mechanism of interaction between radiation and matter, two apparently contradictory aspects of this mechanism have been disclosed. On the one hand, the phenomena of interference, on which the action of all optical instruments essentially depends, claim an aspect of continuity of the same character as that involved in the wave theory of light, especially developed on the basis of the laws of classical electrodynamics. On the other hand, the exchange of energy and momentum between matter and radiation, on which the observation of optical phenomena ultimately depends, claims essentially discontinuous features. These have even led to the introduction of the theory of light-quanta, which in its most extreme form denies the wave constitution of light. At the present state of science it does not seem possible to avoid the formal character of the quantum theory which is shown by the fact that the interpretation of atomic phenomena does not involve a description of the mechanism of the discontinuous processes, which in the quantum theory of spectra are designated as transitions between stationary states of the atom. On the correspondence principle it seems

* Communicated by the Authors.

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nevertheless possible, as it will be attempted to show in this paper, to arrive at a consistent description of optical phenomena by connecting the discontinuous effects occurring in atoms with the continuous radiation field in a somewhat different manner from what is usually done. The essentially new assumption introduced in § 2 that the atom, even before a process of transition between two stationary states takes place, is capable of communication with distant atoms through a virtual radiation field, is due to Slater*. Originally his endeavour was in this way to obtain a harmony between the physical pictures of the electrodynamical theory of light and the theory of light-quanta by coupling transitions of emission and absorption of communicating atoms together in pairs. It was pointed out by Kramers, however, that instead of suggesting an intimate coupling between these processes, the idea just mentioned leads rather to the assumption of a greater independence between transition processes in distant atoms than hitherto perceived. The present paper is the result of a mutual discussion between the authors concerning the possible importance of these assumptions for the elaboration of the quantum theory, and may in various respects be considered as a supplement to the first part of a recent treatise by Bohr, dealing with the principles of the quantum theory, in which several of the problems dealt with here are treated more fully †.

§ 1. *Principles of the Quantum Theory.*

The electromagnetic theory of light not only gives a wonderfully adequate picture of the propagation of radiation through free space, but has also to a wide extent shown itself adapted for the interpretation of the phenomena connected with the interaction of radiation and matter. Thus a general description of the phenomena of emission, absorption, refraction, scattering, and dispersion of light may be obtained on the assumption that the atoms contain electrified particles which can perform harmonic oscillations round positions of stable equilibrium, and which will exchange energy and momentum with the radiation fields according to the classical laws of electrodynamics. On the other

* J. C. Slater, 'Nature,' March 1st, 1924, p. 307.

† N. Bohr, *Zeitschr. für Phys.* xiii. p. 117 (1923). An English translation has recently appeared in the Publications of the Cambridge Philosophical Society under the title: "On the application of the Quantum Theory to atomic structure. I.: The fundamental postulates of the quantum theory." This treatise, which also contains more detailed references to the literature, will in the following be quoted as "P. Q. T."

hand, it is well known that these phenomena exhibit a number of features which are contradictory to the consequences of the classical electrodynamical theory. The first phenomenon where such contradictions were firmly established was the law of temperature radiation. Starting from the classical conception of emission and absorption of radiation by a particle performing harmonic oscillations, Planck found that, in order to obtain agreement with the experiments on temperature radiation, it was necessary to introduce the auxiliary assumption that in a statistical distribution only certain states of the oscillating particles have to be taken into account. For these distinguished states the energy was found to be equal to a multiple of the quantum $h\omega$, where ω is the natural frequency of the oscillator and h is a universal constant. Independent of radiation phenomena, this result obtained, as Einstein pointed out, a direct support from experiments on the specific heat of solids. At the same time, this author put forward his well-known theory of "light-quanta," according to which radiation should not be propagated through space as continuous trains of waves in the classical theory of light, but as entities, each of which contains the energy $h\nu$, concentrated in a minute volume, where h is Planck's constant and ν the quantity which in the classical picture is described as the number of waves passing in unit time. Although the great heuristic value of this hypothesis is shown by the confirmation of Einstein's predictions concerning the photoelectric phenomenon, still the theory of light-quanta can obviously not be considered as a satisfactory solution of the problem of light propagation. This is clear even from the fact that the radiation "frequency" ν appearing in the theory is defined by experiments on interference phenomena which apparently demand for their interpretation a wave constitution of light.

In spite of the fundamental difficulties involved in the ideas of the quantum theory, it has nevertheless been possible to a certain extent to apply these conceptions, combined with information on the structure of the atom derived from other sources, to the interpretation of the results of investigations of the emission and absorption spectra of the elements. This interpretation is based on the fundamental postulate: that an atom possesses a number of distinguished states, the so-called "stationary states," which are supposed to possess a remarkable stability, for which no interpretation can be derived from the concepts of classical electrodynamics. This stability comes to light in the circumstance that any change of the state of the atom must consist of a

complete process of transition from one of these stationary states to another. The postulate obtains a connexion with optical phenomena through the further assumption that when a transition between two stationary states is accompanied by emission of radiation, this consists of a train of harmonic waves, whose frequency is given by the relation

$$h\nu = E_1 - E_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E_1 and E_2 are the values of the energy of the atom in the initial and in the final state of the process respectively. Inversely it is assumed that the reversed process of transition can take place by illumination with light with this same frequency. The applicability of these assumptions to the interpretation of the spectra of the elements is essentially due to the fact that it has been found possible in many cases to fix the energy in the stationary states of an isolated atom by means of simple rules referring to motions which with a high approximation obey the ordinary laws of electrodynamics (P.Q.T., Ch. I., § 2). The concepts of this theory, however, do not allow us to describe the details of the mechanism underlying the process of transition between the various stationary states.

At the present state of science it seems necessary, as regards the occurrence of transition processes, to content ourselves with considerations of probability. Such considerations have been introduced by Einstein*, who has shown how a remarkably simple deduction of Planck's law of temperature radiation can be obtained by assuming that an atom in a given stationary state may possess a certain probability of a "spontaneous" transition in unit time to a stationary state of smaller energy content, and that in addition an atom, by illumination with external radiation of suitable frequency, may acquire a certain probability of performing an "induced" transition to another stationary state with higher or smaller energy content. In connexion with the conditions of thermal equilibrium between radiation and matter, Einstein further arrived at the conclusion that the exchange of energy by the transition process is accompanied by an exchange of momentum of the amount $h\nu/c$, just as would be the case if the transition were accompanied by the starting or stopping of a small entity moving with the velocity of light c and containing the energy $h\nu$. He concluded that the direction of this momentum for the induced transitions is the same as the direction of

* A. Einstein, *Physikalische Zeitschrift*, xviii. p. 121 (1917).

propagation of the illuminating light-waves, but that for the spontaneous transitions the direction of the impulse is distributed according to probability laws. These results, which were considered as an argument for ascribing a certain physical reality to the theory of light-quanta, have recently found an important application in explaining the remarkable phenomena of the change of wave-length of radiation scattered by free electrons brought to light by A. H. Compton's * investigation on X-ray scattering. The application of probability considerations to the problem of temperature equilibrium between free electrons and radiation suggested by this discovery has recently been successfully treated by Pauli †, and the formal analogy of his results with the laws governing transition processes between stationary states of atoms has been emphasized by Einstein and Ehrenfest ‡.

In spite of the fundamental departure of the quantum theory of atomic processes from a picture based on the ordinary concepts of electrodynamics, the former must in a certain sense ultimately appear as a natural generalization of the latter. This is evident from the condition that in the limit, where we consider processes which depend on the statistical behaviour of a large number of atoms, and which involve stationary states where the difference between neighbouring stationary states is comparatively little, the classical theory leads to conclusions in agreement with the experiments. In the case of emission and absorption of spectral lines, this connexion between the two theories has led to the establishment of the "correspondence principle," which postulates a general conjugation of each of the various possible transitions between stationary states with one of the harmonic oscillation components in which the electrical moment of the atom, considered as a function of the time, can be resolved (P. Q. T., Ch. II., § 2). This principle has afforded a basis for an estimation of probabilities of transition, and thereby for bringing the problem of intensities and polarization of spectral lines in close connexion with the motion of the electrons in the atom.

The correspondence principle has led to comparing the reaction of an atom on a field of radiation with the reaction on such a field which, according to the classical theory of electrodynamics, should be expected from a set of "virtual" harmonic

* A. H. Compton, *Phys. Rev.* xxi. p. 483 (1923). See also P. Debye, *Physikalische Zeitschrift*, xxiv. p. 161 (1923).

† W. Pauli, *Zeitschrift für Phys.* xviii. p. 272 (1923).

‡ A. Einstein and P. Ehrenfest, *Zeitschr. für Phys.* xiv. p. 301 (1923).

oscillators with frequencies equal to those determined by the equation (1) for the various possible transitions between stationary states (P. Q. T., Ch. III., § 3). Such a picture has been used by Ladenburg* in an attempt to connect the experimental results on dispersion quantitatively with considerations on the probability of transitions between stationary states. Also in the phenomenon of interaction between free electrons and radiation, the possibility of applying similar considerations is suggested by the analogy, emphasized by Compton, between the change of wave-length of the scattered rays and the classical Doppler effect of radiation from a moving source.

Although the correspondence principle makes it possible through the estimation of probabilities of transition to draw conclusions about the mean time which an atom remains in a given stationary state, great difficulties have been involved in the problem of the time-interval in which emission of radiation connected with the transition takes place. In fact, together with other well-known paradoxes of the quantum theory, the latter difficulty has strengthened the doubt, expressed from various sides†, whether the detailed interpretation of the interaction between matter and radiation can be given at all in terms of a causal description in space and time of the kind hitherto used for the interpretation of natural phenomena (P. Q. T., Ch. III., § 1). Without in any way removing the formal character of the theory, it nevertheless appears, as mentioned in the introduction, that a definite advance as regards the interpretation of the observable radiation phenomena may be made by connecting these phenomena with the stationary states and the transitions between them in a way somewhat different from that hitherto followed.

§ 2. Radiation and Transition Processes.

We will assume that a given atom in a certain stationary state will communicate continually with other atoms through a time-spatial mechanism which is virtually equivalent with the field of radiation which on the classical theory would originate from the virtual harmonic oscillators corresponding with the various possible transitions to other stationary states. Further, we will assume that the occurrence of

* R. Ladenburg, *Zeitschr. für Phys.* iv. p. 451 (1921). See also R. Ladenburg and P. Reiche, *Naturwissenschaften*, xi. p. 584 (1923).

† Such a view has perhaps for the first time been clearly expressed by O. W. Richardson, 'The Electron Theory of Matter,' 2nd edition, p. 507, Cambridge 1916.

transition processes for the given atom itself, as well as for the other atoms with which it is in mutual communication, is connected with this mechanism by probability laws which are analogous to those which in Einstein's theory hold for the induced transitions between stationary states when illuminated by radiation. On the one hand, the transitions which in this theory are designated as spontaneous are, on our view, considered as induced by the virtual field of radiation which is connected with the virtual harmonic oscillators conjugated with the motion of the atom itself. On the other hand, the induced transitions of Einstein's theory occur in consequence of the virtual radiation in the surrounding space due to other atoms.

While these assumptions do not involve any change in the connexion between the structure of the atom and the frequency, intensity, and polarization of the spectral lines derived by means of the relation (1) and of the correspondence principle, they lead to a picture as regards the time-spatial occurrence of the various transition processes on which the observations of the optical phenomena ultimately depend which in an essential respect differs from the usual concepts. In fact, the occurrence of a certain transition in a given atom will depend on the initial stationary state of this atom itself and on the states of the atoms with which it is in communication through the virtual radiation field, but not on the occurrence of transition processes in the latter atoms.

On the one hand it will be seen that our view, in the limit where successive stationary states differ only little from each other, leads to a connexion between the virtual radiation field and the motion of the particles in the atom which gradually merges into that claimed by the classical radiation theory. In fact neither the motion nor the constitution of the radiation field will in this limit undergo essential changes through the transitions between stationary states. As regards the occurrence of transitions, which is the essential feature of the quantum theory, we abandon on the other hand any attempt at a causal connexion between the transitions in distant atoms, and especially a direct application of the principles of conservation of energy and momentum, so characteristic for the classical theories. The application of these principles to the interaction between individual atomic systems is, on our view, limited to interactions which take place when the atoms are so close that the forces which would be connected with the radiation field on the classical theory are small compared with the conservative parts of the fields of force originating from the electric

charges in the atom. Interactions of this type, which may be termed "collisions," offer, as is well known, remarkable illustrations of the stability of stationary states postulated in the quantum theory. In fact, an analysis of the experimental results based on the theory of conservation of energy and momentum is in agreement with the view that the colliding atoms before as well as after the process will always find themselves in stationary states (P. Q. T., Ch. I., § 4)*. By interaction between atoms at greater distances from each other, where according to the classical theory of radiation there would be no question of simultaneous mutual action, we shall assume an independence of the individual transition processes, which stands in striking contrast to the classical claim of conservation of energy and momentum. Thus we assume that an induced transition in an atom is not directly caused by a transition in a distant atom for which the energy difference between the initial and the final stationary state is the same. On the contrary, an atom which has contributed to the induction of a certain transition in a distant atom through the virtual radiation field conjugated with the virtual harmonic oscillator corresponding with one of the possible transitions to other stationary states, may nevertheless itself ultimately perform another of these transitions.

At present there is unfortunately no experimental evidence at hand which allows to test these ideas, but it may be emphasized that the degree of independence of the transition processes assumed here would seem the only consistent way of describing the interaction between radiation and atoms

* These considerations hold obviously only in so far as the radiation connected with the collisions can be neglected. Although in many cases the energy of this radiation is very small, its occurrence might be of essential importance. This has been emphasized by Franck in connexion with the explanation of Ramsauer's important results regarding collisions between atoms and slow electrons (*Ann. d. Phys.* lxiv. p. 513, lxvi. p. 546 (1922)), from which it seems to follow that in certain cases the electron can pass freely through the atom, without being influenced by its presence. In fact, if in these "collisions" a change in the motion of the electron actually took place, the classical theory would involve so large a radiation, that a rational conjugation of the radiation with the possible transition processes, as claimed by the correspondence principle, could hardly be established (compare F. Hund, *Zs. für Phys.* xiii. p. 241, 1923). On the view presented in this paper, such an explanation might on the one hand be regarded as the more natural, since the origin of radiation is not directly sought in the occurrence of transitions but in the motion of the electron. On the other hand, it must be remembered that we are here dealing with a case where, on account of the large magnitude of the classical reaction of radiation, the theory does not allow a sharp distinction between stationary motion and transition processes.

by a theory involving probability considerations. This independence reduces not only conservation of energy to a statistical law, but also conservation of momentum. Just as we assume that any transition process induced by radiation is accompanied by a change of energy of the atom of the amount $h\nu$, we shall assume, following Einstein, that any such process is also accompanied by a change of momentum of the atom of an amount $h\nu/c$. If the transition is induced by virtual radiation fields from distant atoms, the direction of this momentum is the same as that of the wave propagation in this virtual field. In case of a transition by its own virtual radiation, we shall naturally assume that the change of momentum is distributed according to probability laws in such a way that changes of momentum due to the transitions in other atoms are statistically compensated for any direction in space.

The cause of the observed statistical conservation of energy and momentum we shall not seek in any departure from the electrodynamic theory of light as regards the laws of propagation of radiation in free space, but in the peculiarities of the interaction between the virtual field of radiation and the illuminated atoms. In fact, we shall assume that these atoms will act as secondary sources of virtual wave radiation which interferes with the incident radiation. If the frequency of the incident waves coincides closely with the frequency of one of the virtual harmonic oscillators corresponding to the various possible transitions, the amplitudes of the secondary waves will be especially large, and these waves will possess such phase relations with the incident waves that they will diminish or augment the intensity of the virtual radiation field, and thereby weaken or strengthen its power of inducing transitions in other atoms. Whether it is a diminishing or an augmentation of the intensity which takes place, will depend on whether the virtual harmonic oscillator, which is called into play by the incident radiation, corresponds with a transition by which the energy of the atom is increased or diminished respectively. It will be seen that this view is closely related to the ideas which led Einstein to introduce probabilities of two kinds of induced transitions between stationary states corresponding with an increase or decrease of the energy of the atom respectively. In spite of the time-spatial separation of the processes of absorption and emission of radiation characteristic for the quantum theory, we may nevertheless expect, on our view, a far-reaching analogy with the classical theory of electrodynamics as regards the interaction of the virtual radiation field and the

virtual harmonic oscillators conjugated with the motion of the atom. It seems actually possible, guided by this analogy, to establish a consistent and fairly complete description of the general optical phenomena accompanying the propagation of light through a material medium, which accounts at the same time for the close connexion of these phenomena with the spectra of the atoms of the medium.

§ 3. *Capacity of Interference of Spectral Lines.*

Before we enter more closely on the general problem of the reaction of atoms on a virtual radiation field, responsible for the phenomena accompanying the propagation of light through material media, we shall here briefly consider the properties of the field originating from a single atom, as far as they are connected with the capacity of interference of light from one and the same source. The constitution of this field must obviously not be sought in the peculiarities of the transition processes themselves, the duration of which we shall assume at any rate not to be large compared with the period of the corresponding harmonic component in the motion of the atom. These processes will, on our view, simply mark the termination of the time-interval in which the atom will be able to communicate with other atoms through the corresponding virtual oscillator. An upper limit of the capacity of interference, however, will clearly be given by the mean time interval in which the atom remains in the stationary state representing the initial state of the transition under consideration. The estimation of the time of duration of states based on the correspondence principle has obtained a general confirmation from the well-known beautiful experiments on the duration of the luminosity of high speed atoms emerging from a luminescent discharge into a high vacuum. (Compare P. Q. T., (Ch. II., § 4.) On the present point of view these experiments obtain a very simple interpretation. In fact it will be seen that on this view the variation of the luminosity along the path of the atoms will not depend on the peculiarity of the transitions, but only on the relative number of atoms in the various stationary states in the different parts of the path. If all the emerging atoms have the same speed and are initially in the same state, we must thus expect that for any spectral line conjugated with a transition from this state the luminosity will decrease exponentially along the path at one and the same rate. At present the experimental material at hand is hardly sufficient to test these considerations.

When we ask for the capacity of interference of spectral lines, determined by optical apparatus, the mean time of duration of the stationary states will certainly constitute an upper limit for this capacity, but it must be remembered that the sharpness of a given spectral line which is due to the statistical result of the action from a large number of atoms will depend not only on the lengths of the individual wave trains terminated by the transition processes, but clearly also on any uncertainty in the definition of the frequency of these waves. In view of the way this frequency through relation (1) is related to the energy in the stationary states, it is of interest to note that the above-mentioned upper limit of capacity of interference may be brought in close connexion with the limit of definition of the motion and of the energy in the stationary states. In fact, the postulate of the stability of stationary states imposes an *a priori* limit to the accuracy with which the motion in these states can be described by means of classical electrodynamics, a limit which on our picture is directly involved in the assumption that the virtual radiation field is not accompanied by a continuous change in the motion of the atom, but only acts by its induction of transitions involving finite changes of the energy and the momentum of the atom (P. Q. T., Ch. II., § 4). In the limiting region where the motions in the two stationary states involved in the transition process differ only comparatively little from each other, the upper limit of capacity of interference of the individual wave trains coincides with the limit of definition of the frequency of the radiation determined by (1), if the influence of the lack of definition of the energy in the two states is treated as independent errors. In the general case where the motions in these states may differ considerably from each other, the upper limit of the capacity of interference of the wave trains is closely related with the definition of the motion in the stationary state which forms the starting point of the transition process. Also here we may, however, expect that the observable sharpness of the spectral lines will be determined according to relation (1) by adding the effect of any possible lack of definition of the energy in the stationary state terminating the transition process to the effect of the lack of definition in the starting state in a similar way as independent errors. Just this influence of the lack of definition of both stationary states on the sharpness of a spectral line makes it possible to ensure the reciprocity which will exist between the constitution of a line when appearing in an emission and in an absorption spectrum, and which is claimed by the

condition for thermal equilibrium expressed by Kirchhoff's law. In this connexion it may be remembered how the apparent deviations from this law exhibited by the remarkable difference often shown by the structure of the emission and the absorption spectra of an element as regards the number of lines present are directly accounted for on the quantum theory when account is taken of the difference in the statistical distributions of the atoms over the various stationary states under different external conditions.

A problem closely related to the sharpness of spectral lines originating from atoms under constant external conditions, is the problem of the spectrum to be expected from atoms under the influence of external forces which vary considerably within a time-interval of the same order of magnitude as the mean duration of the stationary states. Such a problem is met with in certain of the experiments by Stark on the influence of electric fields on spectral lines. In these experiments the emitting atoms move with large velocities, and the time-intervals in which they pass between two points where the intensity of the electric field differs very much, are only a small fraction of the mean time of duration of the stationary states connected with the investigated spectral lines. Nevertheless Stark found that, except for a Doppler effect of the usual kind, the radiation from the moving atoms was influenced by the electric field at any point of the path in the same way as the radiation from resting atoms subject to the constant action of the field at this point. While, as emphasized by various authors*, the interpretation of this result obviously presents difficulty on the usual quantum theory description of the connexion between radiation and transition processes, it is clear that Stark's results are in conformity with the picture adopted in this paper. In fact, during the passing of the atoms through the field, the motion in the stationary states changes in a continuous way, and in consequence also the virtual harmonic oscillators corresponding with the possible transitions. The effect of the virtual radiation field originating from the moving atoms will therefore not be different from that which would occur if the atoms along their whole path had moved in a field of constant intensity, at any rate if—as in Stark's experiments—the radiation originating from the other parts of their paths is prevented from reaching those parts of the apparatus on which the observation of the phenomenon depends. In a

* Compare K. Försterling, *Zeitschr. für Phys.* x. p. 387 (1922), A. J. Dempster, *Astrophys. Journ.* lvii. p. 193 (1923).

problem of this kind it will also be seen how a far reaching reciprocity in the observable phenomena of emission and absorption is ensured on account of the symmetry exhibited by our picture as regards the coupling of the radiation field with the transition processes in the one or in the other direction.

§ 4. *Quantum Theory of Spectra and Optical Phenomena.*

Although on the quantum theory the observation of the optical phenomena ultimately depends on discontinuous transition processes, an adequate interpretation of these phenomena must, as already emphasized in the introduction, nevertheless involve an element of continuity similar to that exhibited by the classical electrodynamical theory of the propagation of light through material media. On this theory the phenomena of reflexion, refraction, and dispersion are attributed to a scattering of light by the atom due to the forced vibration in the individual electric particles, set up by the electromagnetic forces of the radiation field. The postulate of the stability of stationary states might at first sight seem to involve a fundamental difficulty on this point. The contrast, however, was to a certain extent bridged over by the correspondence principle, which, as mentioned in § 1, led to comparing the reaction of an atom on a radiation field with the scattering which, according to the classical theory, would arise from a set of virtual harmonic oscillators conjugated with the various possible transitions. It must still be remembered that the analogy between the classical theory and the quantum theory as formulated through the correspondence principle is of an essentially formal character, which is especially illustrated by the fact that on the quantum theory the absorption and emission of radiation are coupled to different processes of transition, and thereby to different virtual oscillators. Just this point, however, which is so essential for the interpretation of the experimental results on emission and absorption spectra, seems to afford a guidance as regards the way in which the scattering phenomena are related with the activity of the virtual oscillators concerning emission and absorption of radiation. In a later paper it is hoped to show how on the present view a quantitative theory of dispersion resembling Ladenburg's theory can be established*. Here we shall confine ourselves to emphasizing once more the continuous character of the optical phenomena,

* *Note added during the proof.* The outline of such a theory is briefly described by Kramers in a letter to 'Nature' published in April.

which seemingly does not permit an interpretation based on a simple causal connexion with transition processes in the propagating medium.

An instructive example of these considerations is offered by the experiments on absorption spectra. In fact, the pronounced absorption by monatomic vapours for light of frequencies coinciding with certain lines in the emission spectra of the atoms strictly cannot be said, as often done for brevity, to be caused by the transition processes which take place in the atoms of the vapour induced by wave trains in the incident radiation possessing the frequencies of the absorption lines. The appearance of these lines in the spectroscopic is due to the decrease of the intensity of the incident waves in consequence of the peculiarities of the secondary spherical wavelets set up by each of the illuminated atoms, while the induced transitions appear only as an accompanying effect by which a statistical conservation of energy is ensured. The presence of the secondary coherent wave-trains is at the same time responsible for the anomalous dispersion connected with the absorption lines, and is especially clearly shown by the phenomenon, discovered by Wood*, of selective reflexion from the wall of a vessel containing metallic vapour under sufficiently high pressure. The occurrence of induced transitions between stationary states is on the other hand directly observed in the fluorescent radiation, which for an essential part originates from the presence of a small number of atoms which through the illumination have been transferred to a stationary state of higher energy. As is well known, the fluorescent radiation can be suppressed through the admixture of foreign gases. As regards the part played by atoms in the higher stationary states this phenomenon is explained by collisions which cause a considerable increase of the probability of the atoms to return into their normal state. At the same time any part of the fluorescent radiation due to the coherent wavelets will, through the admixture of foreign gases, just as the phenomena of absorption, dispersion, and reflexion, undergo such changes as can be brought in connexion with a broadening of the spectral lines†. It will be seen that a view on absorption phenomena differing essentially from that just described can hardly be maintained, if it can be shown that the selective absorption of spectral lines is a phenomenon qualitatively independent of the intensity of the

* R. W. Wood, *Phil. Mag.* xxiii, p. 689 (1915).

† See for instance Chr. Fichtbauer and G. Joos, *Physik. Zeitschr.* xxiii, p. 73 (1922).

source of radiation, in a similar way to what has already been found to be the case for the usual phenomena of reflexion and refraction, whose transitions in the medium do not occur to a similar extent (compare P. Q. T., Ch. III., § 3).

Another interesting example is offered by the theory of the scattering of light by free electrons. As has been shown by Compton by means of reflexion of X-rays from crystals, this scattering is accompanied by a change of frequency, different in different directions, and corresponding with the constitution of the radiation which on the classical theory would be emitted by an imaginary moving source. As mentioned, Compton has reached a formal interpretation of this effect on the theory of light-quanta by assuming that the electron may take up a quantum of the incident light and simultaneously re-emit a light-quantum in some other direction. By this process the electron acquires a velocity in a certain direction, which is determined, just as the frequency of the re-emitted light, by the laws of conservation of energy and momentum, an energy of $h\nu$ and a momentum $h\nu/c$ being ascribed to each light-quantum. In contrast to this picture, the scattering of the radiation by the electrons is, on our view, considered as a continuous phenomenon to which each of the illuminated electrons contributes through the emission of coherent secondary wavelets. Thereby the incident virtual radiation gives rise to a reaction from each electron, similar to that to be expected on the classical theory from an electron moving with a velocity coinciding with that of the above-mentioned imaginary source and performing forced oscillations under the influence of the radiation field. That in this case the virtual oscillator moves with a velocity different from that of the illuminated electrons themselves is certainly a feature strikingly unfamiliar to the classical conceptions. In view of the fundamental departures from the classical space-time description, involved in the very idea of virtual oscillators, it seems at the present state of science hardly justifiable to reject a formal interpretation as that under consideration as inadequate. On the contrary, such an interpretation seems unavoidable in order to account for the effects observed, the description of which involves the wave-concept of radiation in an essential way. At the same time, however, we shall assume, just as in Compton's theory, that the illuminated electron possesses a certain probability of taking up in unit time a finite amount of momentum in any given direction. By this effect, which in the quantum theory takes the place of the continuous transfer of momentum to the electrons which on the classical

theory would accompany a scattering of radiation of the type described, a statistical conservation of momentum is secured in a way quite analogous to the statistical conservation of energy in the phenomena of absorption of light discussed above. In fact, the laws of probability for the exchange of momentum by interaction of free electrons and radiation derived by Pauli are essentially analogous to the laws governing transition processes between well-defined states of an atomic system. Especially the considerations of Einstein and Ehrenfest, referred to in § 1, are suited to bring out this analogy.

A problem similar to that of the scattering of light by free electrons is presented by the scattering of light by an atom, even in the case where the frequency of the radiation is not large enough to induce transitions by which an electron is wholly removed from the atom. In fact, in order to secure statistical conservation of momentum, we must, as emphasized by various authors*, assume the occurrence of transition processes by which the momentum of the scattering atom changes by finite amounts without, however, the relative motion of the particles of the atom being changed, as in transition processes of the usual type considered in the spectral theory. It will also be seen, on our picture, that transition processes of the type mentioned will be closely connected with the scattering phenomena, in a way analogous with the connexion of the spectral phenomena with the transition processes by which the internal motion of the atom undergoes a change. Due to the large mass of the atomic nucleus the velocity change which the atom undergoes by these transitions is so small, that it will not have a perceptible effect on the energy of the atom and the frequency of the scattered radiation. Nevertheless, it is of principal importance that the transference of momentum is a discontinuous process, while the scattering itself is an essentially continuous phenomenon, in which all the illuminated atoms take part, independent of the intensity of the incident light. The discontinuous changes in momentum of the atoms, however, are the cause of the observable reactions on the atoms described as radiation pressure. This view fulfils clearly the conditions for thermal equilibrium between a (virtual) radiation field and a reflecting surface, derived by Einstein† and considered as an argument for the light-quantum theory. At the same time it needs hardly be

* W. Pauli, *loc. cit.*; A. Smekal, *Naturwissenschaften*, xi. p. 875 (1923).

† A. Einstein, *Phys. Zeitschr.* x. p. 817 (1909).

emphasized that it is also consistent with the apparent continuity exhibited by actual observations on radiation pressure. In fact, if we consider a solid, a change of $h\nu/c$ in its total momentum will be totally imperceptible, and for visible light even vanishingly small compared with the irregular changes of this momentum of a body in thermal equilibrium with the surroundings. In the discussion of the actual experiments it may, however, be noted at the same time, that the frequency of the occurrence of such processes may often be so large that the problem arises whether the time involved in the transitions themselves can be neglected, or, in other words, whether the limit has been reached inside which the formulation of the principles of the quantum theory can be maintained (compare P. Q. T., Ch. II., § 5).

The last considerations may illustrate how our picture of optical phenomena offers a natural connexion with the ordinary continuous description of macroscopic phenomena for the interpretation of which Maxwell's theory has shown itself so wonderfully adapted. The advantage in this respect of the present formulation of the principles of the quantum theory over the usual representation of this theory will perhaps be still more clearly illustrated if we consider the phenomenon of emission of electromagnetic waves, say from an antenna as used in wireless telegraphy. In this case no adequate description of the phenomenon is offered on the picture of emission of radiation during separate successive transition processes between imaginary stationary states of the antenna. In fact, when the smallness of the energy changes by the transitions, and the magnitude of the energy radiation from the antenna per unit time, are taken into account, it will be seen that the duration of the individual transition processes can only be an exceedingly small fraction of the period of oscillation of the electricity in the antenna, so that there would be no justification in describing the result of one of these processes as the emission of a train of waves of this period. On the present view, however, we will describe the action of the oscillation of the electricity in the antenna as producing a (virtual) radiation field which through probability laws again induces changes in the motion of the electrons which may be regarded as continuous. In fact, even if a distinction between different energy steps $h\nu$ could be kept upright, the size of these steps would be quite negligible compared with the energy associated with the antenna. It will in this connexion be observed that the

emphasizing of the "virtual" character of the radiation field, which at the present state of science seems so essential for an adequate description of atomic phenomena, automatically loses its importance in a limiting case like that just considered, where the field, as regards its observable interaction with matter, is endowed with all the attributes of an electromagnetic field in classical electrodynamics.

Institute for Theoretical Physics, Copenhagen,
January 1924.

LXXVII. *The Effect of an Electric Current on the Motion of Mercury Globules in Dilute Sulphuric Acid, and its Bearing on the Problem of the Electrolytic Double Layer.* By J. E. P. WAGSTAFF, M.A., Fellow of St. John's College, Cambridge, Lecturer in Physics at the University of Leeds*.

Introduction.

IT was pointed out to me in 1920 by Professor R. Whiddington that when small globules of mercury are injected into a tube of sulphuric acid, inclined at a small angle to the horizontal, the globules can be made to move up the tube against gravity on sending a current in a particular direction through the acid. During the last two years I have made a detailed study of the motion of these mercury globules, and the results obtained and the conclusions reached to date seem of sufficient importance and general interest to justify their publication.

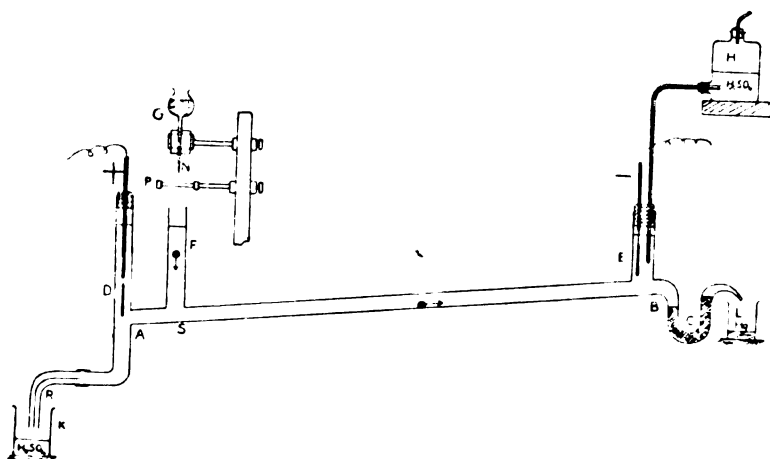
Apparatus and Method.

The tube AB (fig. 1) used for these experiments has an overall length of 50 cm. approximately and an internal diameter 0.35 cm. It is fitted with three side tubes D, E, and F of approximately the same diameter. The tubes D and E are supplied with electrodes of stiff platinum foil, which are brought into communication with the external circuit by sealing them into thin glass tubes containing mercury. The drops are formed at the end of a fine capillary tube N in hydrostatic communication with a reservoir G, the level of the mercury in which is kept constant, and they enter the apparatus through the tube F. As determinations of the masses of the mercury drops have to be made from time to time, it is convenient to have a metal ring at P for

* Communicated by the Author.

supporting the dish used to collect the drops. The U-piece C, which is initially filled with mercury, serves as a receptacle for the globules at the end of their course. At the beginning of each experiment, the mercury ejected into the beaker L is emptied back into G and used over again. In order to obtain consistent readings, it has been found necessary during the experiments to renew the acid continuously. This is best arranged by allowing a very slow stream of acid (1 drop per sec.) to enter at E and leave at R, the rates of inflow and outflow being carefully regulated until the level of the liquid in the tube shows no variation with time.

Fig. 1.



The apparatus is mounted on a substantial wooden board, which can turn about a horizontal axis so as to tilt the tube to any desired extent. When a current is passed through the acid from D to E, the globules are observed to rise up the tube and fall into B; with a current in the opposite direction the drops move down the tube. The general characteristics of the motion may be summarized thus:—

The velocity of a drop remains constant during its progress from S to B, and can thus be measured by the time taken to move over a given length of the tube. For a given potential difference between D and E, the velocity varies with the radius of the drop in accordance with the Stokes-Ladenburg law of viscosity.

Moreover, the velocity is a linear function of the potential difference between the ends of the tube. In confirmation of

this, it is interesting to notice that the globules show no tendency to travel up the tube under the action of an alternating current.

When the electrolyte is replaced by a non-conducting liquid, the motion of a mercury drop under gravity is unaffected by a potential difference applied between D and E. Mechanical forces, such as arise when a conducting sphere is placed in an electrostatic field, can therefore be neglected in any theoretical considerations of this phenomenon.

In a preliminary set of observations, three determinations of the variation of velocity with potential difference have been made for two different tubes. Each velocity quoted in the following short table is the mean of twelve observations.

TABLE I.

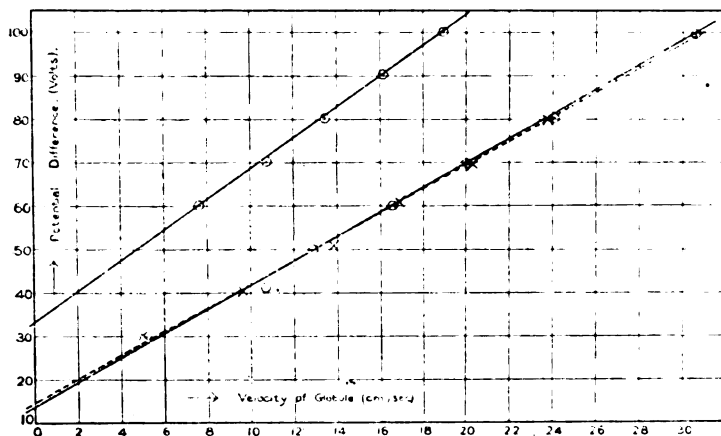
Distance l between electrodes. cm.	Inclination θ of tube to horizontal.	Radius of drop. cm.	Potential difference V between electrodes. Volts.	Velocity v of drop. cm./sec.	$\bar{V}/l \sin \theta$.
47	$\sin^{-1} 0.0266$	0.08786	41	10.75	11.2
			50	12.97	
			60	16.65	
			70	20.04	
			80	24.0	
			100	30.6	
47	$\sin^{-1} 0.02291$	0.1208	30	5.12	12.5
			40	9.56	
			51	13.91	
			61	16.9	
			69.5	20.26	
			80	23.72	
69	$\sin^{-1} 0.04534$	0.0691	100.5	27.23	10.4
			60	7.64	
			70	10.76	
			80	13.5	
			90	16.16	
			100	18.95	

The numbers given in columns 4 and 5 indicate a linear relationship between V and v (see fig. 2). If V is the value of V corresponding to $v=0$ (extrapolated from the appropriate curve), the values of the quantity $V/l \sin \theta$ are approximately constant for the three experiments (column 6, Table I.)

In order to study in greater detail the effect of the size of globule, a more comprehensive set of observations is now

undertaken, the tilt θ of the tube being maintained constant throughout the series. The applied potential difference is

Fig. 2.



varied from 20 to 50 volts in steps of 5 volts. The results are given below (Table II.).

In fig. 3 the numbers given in columns 2 and 3 are plotted and, as before, v is seen to be a linear function of V . The slope of the line increases uniformly as the size of the drop diminishes. Also the lines have a common point of intersection at $v=0$, $V=15.5$ volts. At this voltage, the force in the direction SB exactly balances the resolved part of the weight for any size of drop. For voltages greater than this, drops of all sizes are urged upwards; for smaller voltages the drops move downwards.

Theory.

According to the theory of Nernst*, when a metal comes into contact with a solution, a transference of ions takes place in accordance with the respective osmotic and solution pressures. If the circuit is not completed, this transference of ions will produce a P.D. at the contact of the metal and solution, which will increase as the transference of ions continues until a limit is reached at which further transference is prevented. In the case of a mercury drop in contact with sulphuric acid, the mercury ions in solution pass to the drop since the solution pressure of the mercury is extremely small

* Nernst, *Zeitschr. Phys. Chem.* iv. p. 129 (1889).

TABLE II.

Sulphuric Acid N/10.

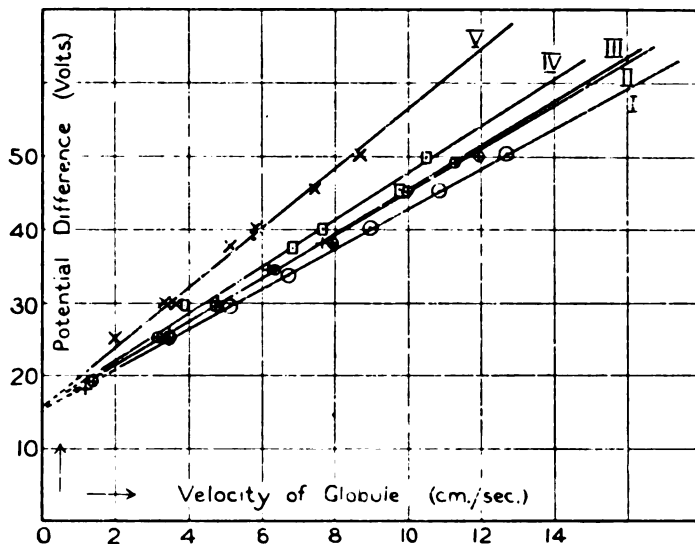
Distance l between electrodes = 47 cm.Inclination θ of tube to horizontal = $\sin^{-1} \cdot 02173$.

Radius a of drop. cm.	Potential difference V between electrodes. — Volts.	Velocity v of drop. cm./sec.
·1072	20	→
	25	3·506
	29·5	5·117
	33·5	6·74
	40	8·91
	45·5	10·85
	50	12·69
·09189	19	1·430
	25	3·16
	29·5	4·74
	34·5	6·35
	38	7·95
	45	9·97
	49	11·29
·09055	25 (Repeat)	3·16
	18	1·15
	25	3·48
	29·5	4·80
	34·5	6·19
	38	7·63
	44·5	9·76
·08722	50	11·95
	20	→
	25	3·042
	29·5	3·86
	37·5	6·861
	40	7·67
	45·5	9·78
·06662	50	10·52
	25 (Repeat)	3·042
	19	→
	25	2·021
	29·5	3·63
	37·5	5·18
	40	5·87
	45·5	7·445
	50	8·694
	29·5 (Repeat)	3·415

→ indicates a distinct upward tendency difficult to measure.

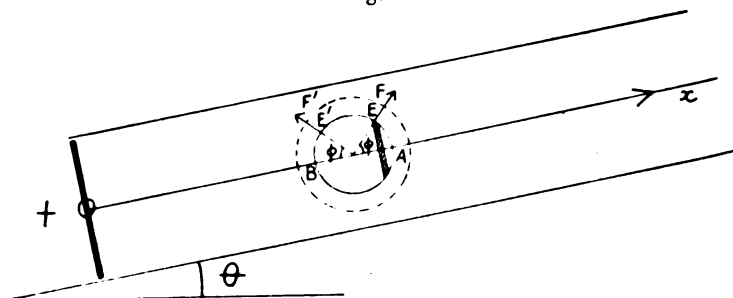
and is less than the osmotic pressure for even a very dilute solution. The mercury thus becomes positively charged, and

Fig. 3.



the whole of the charge so accumulated is derived from ions originally in solution. This positively-charged conductor repels positive ions and attracts an outer shell of negative ions to form what is to all intents and purposes a small spherical condenser of molecular thickness, the difference in

Fig. 4.



potential between the plates of which constitutes the contact potential difference V_0 . Let AB (fig. 4) represent a spherical drop of mercury of radius a surrounded by a concentric outer shell (radius $a+d$) of negative ions. d is thus the

thickness of the double layer. Let $\frac{\partial V}{\partial x}$ represent the gradient of the externally applied potential, x being measured from the positive electrode. If the gradient is uniform, $\frac{\partial V}{\partial x} = V/l$, where V is the P.D. between the electrodes distance l apart.

The mechanical force per unit area of a charged conductor is $2\pi\sigma^2$ along the direction of the normal, where σ is the density of the charge.

The difference of potential between E and F (fig. 4)

$$= V_0 + \frac{\partial V}{\partial x} d \cos \phi = Q/C = 4\pi\sigma_E \cdot d,$$

where σ_E is the density of charge at E, and $C = a^2/d$. The mechanical force, resolved along Ox, on a sector of the sphere making an angle ϕ with the axis Ox is given by

$$F_1 = \left(V_0 + \frac{\partial V}{\partial x} d \cos \phi \right)^2 2\pi a^2 \sin \phi \cos \phi d\phi / 8\pi d^2.$$

Similarly, for the symmetrically situated points E', F',

$$4\pi\sigma_E d = V_0 - \frac{\partial V}{\partial x} \cdot d \cos \phi,$$

and the force F_2 on the corresponding sector resolved along Ox is given by

$$F_2 = \left(V_0 - \frac{\partial V}{\partial x} d \cos \phi \right)^2 2\pi a^2 \sin \phi \cos \phi d\phi / 8\pi d^2.$$

$$F_1 + F_2 = \frac{a^2 V_0}{d} \cdot \frac{\partial V}{\partial x} \sin \phi \cos^2 \phi d\phi,$$

and the total force on the sphere in the direction Ox due to the charge on its surface

$$\begin{aligned} &= \frac{a^2 V_0}{d} \cdot \frac{\partial V}{\partial x} \int_0^{\pi/2} \sin \phi \cos^2 \phi d\phi, \\ &= \frac{a^2 V_0}{3d} \cdot \frac{\partial V}{\partial x}, \end{aligned}$$

where V_0 and V are expressed in E.S.U. If V_0 and V are given in volts, the total force becomes

$$\frac{a^2 V_0}{3d \times 9 \times 10^4} \times \frac{\partial V}{\partial x}.$$

The resultant force along Ox acting on the sphere is

$$a^2 V_0 \frac{\partial V}{\partial x} - \frac{4}{3} \pi a^3 (\rho - \lambda) g \sin \theta,$$

$$3ld \times 9 \times 10^4 - \frac{4}{3} \pi a^3 (\rho - \lambda) g \sin \theta,$$

and for steady motion this is a measure of the force of viscosity which, for small velocities, can be written proportional to v .

Therefore

$$\frac{a^2 V_0 V}{3ld \cdot l \times 9 \times 10^4} - \frac{4}{3} \pi a^3 (\rho - \lambda) g \sin \theta = \kappa v. \quad (1)$$

When $V = 15.5$ volts, $v = 0$;

therefore

$$\frac{a^2 V_0 15.5}{3ld \times 9 \times 10^4} = \frac{4}{3} \pi a^3 (\rho - \lambda) g \sin \theta. \quad (2)$$

Substituting in (1),

$$V - 15.5 = \frac{46.5 \kappa v}{4 \pi a^3 (\rho - \lambda) g \sin \theta} = v \tan \psi, \quad (3)$$

where ψ is the slope of the appropriate line in fig. 3. The quantity κ is not in this case numerically equal to $6\pi\mu a \times (1 + 2.4a/R)$, where μ is the coefficient of viscosity of the acid and R the inner radius of the tube, since the drop is not moving along the axis of the tube but in close proximity with the boundary, and also the motion may include rotation as well as a simple translation. Equation (3) clearly demonstrates a linear relationship between v and V , and also indicates that $\tan \psi$ increases as a diminishes.

Returning to equation (2), which expresses the condition for equilibrium of the drop, d can be calculated for given values of a , l , and θ .

In fact,

$$d = V_0 \frac{\partial V}{\partial x} \left| \frac{4 \pi a (\rho - \lambda) g \sin \theta \times 9 \times 10^4}{1.01 \times 10^{-8} \text{ cm.}}, \right.$$

when

$a = .1072$ cm., $\frac{\partial V}{\partial x} = 15.5/47$ volts per cm., $\sin \theta = .02173$, and V_0 (the contact difference of potential) is 1 volt (see Table II.).

The theory thus gives a value for d of molecular dimensions which can be taken as confirmatory of the validity of the argument presented.

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Again, since for equilibrium $\frac{\partial V}{\partial x}$ is independent of a (see fig. 3), ad/V_0 is independent of a and equal numerically to 1.089×10^{-9} on substitution in equation (2).

If E is the electrostatic charge on either plate of the small spherical condenser previously defined,

$$E = CV_0 = a^2 V_0 / d = a^3 V_0 / d \times 3 \times 10^2,$$

where V_0 is in volts.

$$\begin{aligned} \text{Therefore } E &= a^3 10^7 / 3.267 \text{ E.S.U.,} \\ &= a^3 e 10^{17} / 15.58, \end{aligned} \quad (4)$$

where e is the electronic charge. The experiments indicate, therefore, that the charge on the drop is directly proportional to the cube of the radius, and for a drop of known size the magnitude of the charge can be calculated. If N is the number of mercury atoms in a surface layer of atomic thickness for a drop of radius a ,

$$N = 4\pi a^2 / (\Delta V)^{2/3} = 1.49 \times 10^{16} a^2,$$

(ΔV) being the volume of a mercury atom.

$$\text{Therefore } E/N = ae/2.321,$$

and for a drop of radius .1072 cm.,

$$E/N = e/21.65,$$

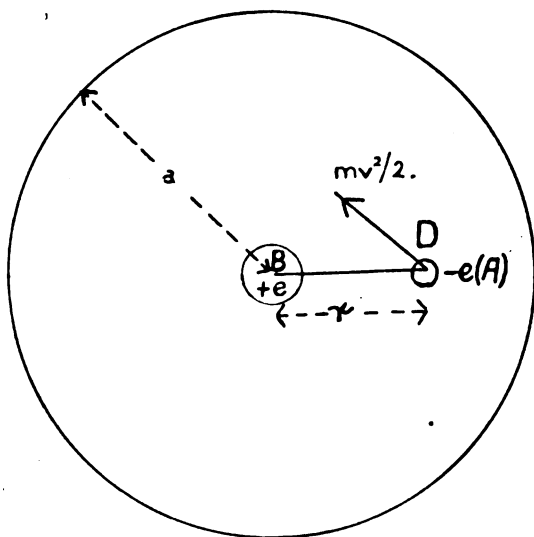
i. e. the equilibrium state requires one mercury ion in the outermost layer to 22 atoms of the mercury surface.

These experimental facts receive theoretical verification as follows:—

Consider a solution containing positively- and negatively-charged ions and neutral molecules. Let B (fig. 5) at any point of the solution be a positively-charged ion of mass large compared with the other ions when it can be regarded as fixed. We wish to find the condition that a negative ion A shall recombine with B, *i. e.* shall describe a closed orbit round B. It will be assumed that the process of recombination is not due to the direct collision between ions, but rather to collisions between ions and neutral molecules. If such a collision between A and a neutral molecule occurs at D ($BD=r$), the condition that the subsequent motion of A shall be confined to closed orbits round B is that the energy ($mv^2/2$) possessed by A after the collision is less than the work required to remove A to an infinite distance. It

will be assumed that at each collision of A with a neutral molecule the previous history is wiped out, and the ion starts out with an amount of energy appropriate at the

Fig. 5.



temperature θ . Thus A will describe a closed orbit round B if

$$mv^2/2 = 3k\theta/2 \leq e^2/r,$$

i. e. $r \leq e^2/3k\theta.$

Thus, if an ion collides with a neutral molecule within a sphere of radius $r = e^2/3k\theta$, the ion is retained by B. If an imaginary sphere of radius a is drawn surrounding B, and r is written equal to βa , then

$$\beta = \frac{e^2}{a} / 3k\theta = w/3k\theta.$$

The negative charge associated with the assemblage of ions in the sphere of radius r captured by B is given by $\frac{4}{3}\pi r^3(-ne)$, where n is the concentration of the negative ions per unit volume. This charge must be identical with $-e$, as the charge $+e$ is only able to reunite with one ion bearing the same charge.

ions in solution, $n = 1.53 \times 10^{15}/\text{c.c.}$ at $\theta = 289^\circ \text{ A.}$ and

Volume occupied by mercury ion
Volume occupied by water molecule $= 2.2 \times 10^7$ at 289° A.

The theory thus indicates that the mercury ions in solution constitute a very small percentage of the total number of molecules present per unit volume.

It has been assumed earlier in the discussion that the energy $mv^2/2$ of a mercury ion is a measure of the temperature,

$$mv^2/2 = 3k\theta/2.$$

Also it is clear that the charge E on the surface of a mercury drop of radius a , suspended in the solution, is stationary when no ion possessing energy $3k\theta/2$ is able to penetrate the double layer a radial distance d , so that

$$\frac{3}{2}k\theta < \alpha Eed/a^2$$

for equilibrium, where α is a constant. Also $E = a^2 V_0/d$, so that $V_0 = 3k\theta/2\alpha e$, or V_0 is the same for drops of all sizes. Hence, since ad/V_0 is constant, the thickness of the electrolytic layer is inversely proportional to the radius of the drop. This result must follow, since the electrostatic field of a uniformly charged spherical conductor is inversely proportional to r^2 ; a small positively-charged drop is therefore able to attract a much larger cluster of negative ions. The size of d is of course limited both as to its maximum and its minimum values by further considerations. The lower limit is fixed by the ultimate size of the negative ion, and the upper limit by the consideration that, on account of thermal agitation, large clusters are liable to be broken up, the outer layers being brushed off by the impacts of other molecules.

In conclusion, returning to equation (6) and substituting e^2/a for w , E is again proportional to a^3 .

E is large when w is small in comparison with $k\theta$. This happens when either θ is large or a is large; thus high temperature and large drops assist the formation of the electrolytic layer.

At normal temperatures, on the other hand, w is much greater than $k\theta$ for sufficiently small values of a . The formation of the electrolytic double layer thus becomes increasingly difficult as the radius of the drop is decreased. In the case of a drop of the dimensions of a mercury ion (10^{-8} cm.), for example, the charge necessary for the formation of the double layer is given by

$$E = 6.7 \times 10^{-2} e \text{ (} e \text{ the electronic charge) :}$$

the non-existence of an electrolytic double layer in the case of drops of atomic size is thus at once explained in terms of the atomicity of electric charge. A critical diameter can be defined, below which no double layer exists. This critical diameter is given by the equation

$$E = e = e \left/ \left(\frac{w}{3k\theta} \right)^3 \right.,$$

$$w/3k\theta = 1,$$

$$e^2/a = 3k\theta/2,$$

or $a = 40\mu\mu.$

Thus for drops of radius less than $40\mu\mu$ the double layer is absent. Working with thin films, Rücker and Reinold* found there are never any parts of the film with a thickness anywhere between $12\mu\mu$ and something between 45 and $95\mu\mu$; films whose thicknesses are within this range are unstable. The two problems may not be unassociated.

Further experiments are in progress, and will form the subject of a subsequent paper.

University of Leeds,
Jan. 1st, 1924.

Note added Jan. 28th, 1924.

A simple explanation of the working of a capillary electrometer of the Lippmann pattern can also be given on much the same lines as the above. When a small potential difference V is applied to the electrodes of a Lippmann capillary electrometer it will be assumed, provided no electrolysis of the solution ensues, that the whole of such impressed potential difference is concentrated in a layer of molecular thickness adjoining the mercury surface. In view of the small solution pressure of mercury ions such an assumption does not seem unreasonable.

An electrolytic double layer of thickness d and potential difference $V + V_0$, V_0 being the natural contact potential difference between the mercury and the solution, is thus established in the solution. The density of charge σ on the inner shell of this layer is given by $4\pi a^2\sigma = (V + V_0)a^2/d$ for a tube of radius a , and the pull F_1 on the surface in the direction of the axis of the tube is

$$F_1 = 2\pi^2 a^2 \sigma^2 = a^2 (V + V_0)^2 / 8d^2.$$

* Rücker & Reinold, Phil. Trans. clxxvii. pt. ii. p. 627 (1886).

Similarly the density σ_1 of the negative charge on the outer shell is given by $4\pi(a+d)^2\sigma_1 = (V + V_0)a^2/d$, and the pull F_2 on this surface along the axis of the tube is

$$F_2 = -a^4(V + V_0)^2/8d^2(a+d)^2.$$

The net pull on the layer along the axis is

$$F_1 + F_2 = (V + V_0)^2 a/4d.$$

Again suppose that when the system has attained the equilibrium state, the meniscus is at a distance X along the tube, the origin of coordinates being chosen at the point of intersection of the axis of the capillary with the level of the mercury in the reservoir. X is defined by the condition that for a further advance δX of the meniscus along the tube, the virtual work is zero.

$$i. e. \frac{(V + V_0)^2 a}{4d} \delta X - 2\pi a T_0 \cos \phi \delta X - \pi a^2 (\rho - \lambda) g X \sin \theta \delta X = 0$$

. . . . (I.)

T_0 and ϕ being the surface tension and angle of contact for the mercury-acid surface, ρ and λ the densities of the mercury and acid respectively, and θ the inclination of the tube to the horizontal. When the externally applied potential V is zero, the value of X say $\bar{X}$ is defined by the equation

$$\frac{V_0^2 a}{4d} - 2\pi a T_0 \cos \phi = \pi a^2 (\rho - \lambda) g \bar{X} \sin \theta \quad . \quad (II.)$$

This corresponds to the normal position of the mercury in the capillary. The change in position of the mercury-acid meniscus corresponding to an applied potential V is given by

$$X - \bar{X} = (V + V_0^2 - V_0^2)/4\pi a d (\rho - \lambda) g \sin \theta,$$

which is a parabola giving a minimum value for $X - \bar{X} =$

$$-V_0^2/4\pi a d (\rho - \lambda) \sin \theta g, \quad . \quad . \quad (III.)$$

at $V = -V_0$. The thread of mercury thus recedes to its minimum position when the applied potential difference just neutralizes the contact potential difference. If d be evaluated from (III.) for an actual set of observations, it is of the order 10^{-8} cm. Finally, if the minimum value of $X - \bar{X}$ is independent of the radius of the capillary tube, ad/V_0 is constant as suggested by the experiments with the moving mercury globules.

LXXVIII. *The Adjustment of Observations.*

By NORMAN CAMPBELL, *Sc.D.**

Summary.

1. PROFESSOR EDGEWORTH has recently suggested the use of medians, as an alternative to least squares (L.S.), for reducing observations involving two variables, on account of their superior facility. Opportunity is therefore taken to press once more the claims of the method of zero sum (Z.S.), which is even simpler.

2. The method is described again with special reference to two variables.

3. Some more examples are given, including those of Prof. Edgeworth.

4. It is urged again that there is no reason to believe that Z.S. is necessarily inferior in accuracy to L.S., or

5. If it is inferior, that the difference is significant.

6. Some methods are discussed whereby it might be possible to decide experimentally whether Z.S. is inferior to L.S. Such applications of them as have been made do not indicate any difference between the two methods appreciable to experiment.

1. Prof. Edgeworth's paper on "the Use of Medians for reducing Observations" (Phil. Mag. xlv. p. 1074, 1923), encourages me to press once more the claims of the method of Zero Sum (Z.S.) which was described in Phil. Mag. xxxix. p. 177, 1920. For Prof. Edgeworth, while holding that the method of Least Squares (L.S.) is always the best of all, urges that in some cases the method of medians may be employed on account of its greater convenience. If it is once admitted that convenience may even be a factor determining the choice of method, the claims of Z.S. are overwhelming; in convenience it surpasses far all proposed arithmetical methods, and often even graphical methods. And yet, so far as I know, the method is not habitually used by anyone but myself.

2. Perhaps it is permissible to describe the method once more, confining attention this time to the form that it takes in the vast majority of physical problems, when the number of variables and of constants to be determined is 2. In such

* Communicated by the Author.

problems, measurements have been made on each of two magnitudes, x , y , which are known (or assumed) to be related by the linear equation

$$y = a + bx. \quad (1)$$

A measurement of x with its associated y constitutes a single observation. The problem is to find values of a and b which make the observations fit closely to the equation (1); it is solved by Z.S. as follows:

(1) Arrange the n observations in the order of the magnitude of that variable which is intentionally changed in passing from one observation to another. If the equation (1) is of the form given, this magnitude will usually be x , and the observations are to be arranged in ascending or descending order of x . It is usually possible to enter the observations in this order in the note-book; if this is done, the trouble of writing them out again is saved.

(2) Divide the observations centrally into two halves, the first half constituting one set, the second another. If n is odd, halve the central observation and count one half in each set.

(3) In each set add together all the x 's and all the y 's, forming the sums $\Sigma_1 x$, $\Sigma_1 y$ for the first set, and $\Sigma_2 x$, $\Sigma_2 y$ for the second.

(4) Solve for a and b the two simultaneous equations

$$\left. \begin{aligned} \Sigma_1 y &= \frac{n}{2} \cdot a + b \cdot \Sigma_1 x \\ \Sigma_2 y &= \frac{n}{2} \cdot a + b \cdot \Sigma_2 x \end{aligned} \right\} \dots \dots \dots (2)$$

The resulting values of a and b are those required.

(5) The arithmetic is so simple that "checks" other than repetition are seldom required. But if for any reason the residuals (*i. e.*, the difference between the observed y 's and those calculated from (1) by the use of the deduced values of a and b) have to be computed, a check can be obtained by observing that the sums of the residuals in each set must be accurately zero, except in so far as figures have been rounded off in computing.

If the observations are arranged originally in the required order, it is quicker to find a and b arithmetically than by the usual graphical process. The ease of the method can be

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realized from the fact that Ex. IV. below, involving 54 observations, was worked out (apart from computing the residuals) during a train journey of 20 minutes, without the use of tables and writing on nothing but the margin of the printed page.

3. A few examples may now be given. Of these, only one is in the least typical of normal physical problems, namely Example IV. ; it is chosen because it is so typical. The other three are those of which the figures are given by Prof. Edgeworth. They are included only to show that the method works and gives at least a good approximation in the most unlikely examples. In Examples II. & III., in the absence of the necessary information, the observations, for the purpose of division into sets, have been arranged in the order in which they are printed. Prof. Edgeworth's result has been added to his own examples ; but, since the median method is not discussed here, it is omitted from Ex. IV., to which it is not easily applicable. In each example, the residuals and the sum of their squares are given for each method of reduction*.

EXAMPLE I.

Edgeworth's Ex. 1.

L.S.	$a=1.784 \pm 0.039$	$b=0.369 \pm 0.025$
Z.S.	$a=1.789$	$b=0.396$
Median	$a=1.745$	$b=0.368$

Residuals.

L.S.	Z.S.	Median.
+0.0347	+0.0757	+0.0676
-0.0480	-0.0450	-0.0233
-0.0479	-0.0614	-0.0277
-0.0210	-0.0430	-0.0036
+0.0980	+0.0737	+0.1120
Σr^2	0.0158	0.0184

* Prof. Edgeworth's x and y correspond to my a and b , except as regards a factor common to both. The conventional notation, whereby the constants a and b are represented by x and y , symbols otherwise confined to variables, is confusing. The reason for it is, of course, that, for the purpose of the adjustment of observations, the constants are the unknowns to be determined. In Example I. 0.1669 is clearly a misprint for 1.669.

EXAMPLE II.

Edgeworth's Ex. 3.

L.S.	$a=1.019 \pm 0.332$	$b=0.0153 \pm 0.0203$
Z.S.	$a=0.776$	$b=0.0242$
Median.	$a=0.943$	$b=0.0182$

Residuals.

	L.S.	Z.S.	Median.
	- 9.40	- 8.93	- 9.16
	- 0.33	+ 0.46	0
	+13.66	+14.52	+14.14
	- 6.39	- 6.04	- 6.26
	-27.77	-36.95	-30.53
	+27.87	+20.19	+25.56
	+10.50	+ 8.98	+10.05
	+10.42	+ 7.79	+ 9.63
Σv^2	2083	2208	2102

EXAMPLE III.

Edgeworth's Ex. 5.

L.S.	$a=25533.6 \pm 16.1$	$b=244.3 \pm 32.7$
Z.S.	$a=25537.4$	$b=250.4$
Median.	$a=25406.6$	$b=483.1$

Residuals.

	L.S.	Z.S.	Median.
	+18.07	+ 5.19	+452.72
	+80.54	+ 73.00	+155.19
	-51.96	- 62.09	- 2.16
	-16.28	- 32.08	+ 21.87
	-28.03	-102.34	- 0.05
	+51.32	+ 28.13	+ 38.31
	+99.73	+ 90.29	+ 21.70
Σv^2	23144	29657	231461

EXAMPLE IV.

Zwetsch, *Zeit. f. Phys.* xix. p. 407 (1923).

L.S.	$a=0.0131135 \pm 0.0000093$	$b=0.000000175 \pm 0.00000023$
Z.S.	$a=0.0131045$	$b=0.000000200$

Residuals $\times 10^6$.

L.S.	Z.S.	L.S.	Z.S.	L.S.	Z.S.
+36	+30	-28	-30	-02	+01
-41	-47	+01	-01	-19	-16
+16	+10	+00	-01	-12	-08
-41	-47	-50	-51	+12	+16
-11	-17	-12	-13	+36	+39
-29	-35	+09	+08	+14	+17
+13	+07	+41	+40	-16	-12
-25	-31	+36	+35	+20	+23
+10	-04	+29	+28	-21	-18
+44	+40	+04	+05	-58	-53
-05	-09	-27	-26	+42	+48
-35	-39	-12	-11	+25	+31
+66	+62	+02	+03	-01	+05
-18	-22	-44	-43	+30	+36
-01	-05	-10	-09	+20	+26
+20	+16	-19	-18	-22	-16
+48	+44	-20	-19	+29	+35
+28	+25	-24	-23	-20	-14

 Σv^2 (L.S.) 41740×10^{-12} (Z.S.) 42982×10^{-12} .

The examples confirm the results indicated by those given previously and by the numerous examples arising from my own experiments—namely, that the difference between the Z.S. and L.S. values never much exceeds the probable error of the latter, even though n is small, systematic error is suspected, and the conditions are generally unfavourable to agreement. Further, since a difference of as much as the p.e. may seem serious, it should be pointed out that this way of expressing the difference is misleading. In the Zwetsch example, which alone is typical of the method, though the difference between Z.S. and L.S. is about equal to the p.e. for both a and b , the difference in Σv^2 is less than 3 per cent., and the difference in the “corrected refraction” (which it is the object of the experiment to find) is very much less than the p.e. For this quantity L.S. gives 291.41 ± 0.39 , while Z.S. gives 291.45.

4. But though the differences between the values given by L.S. and Z.S. are small in these examples, and in all the very much greater number that I have examined, it is possible that they are significant. If, as seems still to be believed generally, L.S. is more accurate than any other

method, it may be necessary sometimes, if not always, to face the greater amount of work which it entails.

In the previous paper, and in my 'Physics,' Chs. xvi. and xvii., reasons have been given for thinking that the general belief is unfounded; and I have little to add to what has been said already and nothing to subtract from it*. But I would venture to put the position again. It is not urged that L.S. is wrong or that Z.S. is right; for I do not think that in the adjustment of observations any method can be definitely right; there is always a margin of uncertainty which, from the very nature of the case, it is impossible to abolish. What I do maintain is that there is no reason to believe that L.S. is more often right than Z.S. Again, it is not denied that L.S. is a valid logical deduction from certain premisses—though mathematicians do not seem wholly agreed from what premisses it is deducible. Given those premisses, L.S. is certainly right and Z.S. wrong. But I deny that there is any evidence that premisses from which L.S. can be deduced are true in the experimental sense.

If propositions having any bearing on experiment are to be deduced from the premisses of a theory of error, those premisses must contain experimental conceptions, or ideas capable of interpretation in terms of experimental conceptions. Such conceptions are involved in the foundations of the orthodox theory of errors in two ways. First, they are involved in the assertion that the "most probable" value is the right value to take for experimental purposes. Those who have not inquired deeply into the matter are apt to forget how very complex and difficult is this idea of "most probable." It is introduced by the fundamental theorem of inverse probability, of which Bayes's theorem is one form.

* *Note added in correction.* I criticised certain of the well-known rules for adjustment according to the Method of L.S. on the ground that, in special cases, they led to absurd results. This criticism has offended greatly Dr. R. M. Stewart (Phil. Mag. xl. p. 217, 1920) and Mr. H. S. Uhler (J. Opt. Soc. Amer. vii. p. 1043, 1923). They admit that the rules quoted are not applicable to these cases; but they maintain that it is not consistent with the principles on which the Method of L.S. is based so to apply them; they give alternative rules based on those principles. But these principles are precisely what I reject; any rules based on them are, for me, purely empirical; and I can admit no error in comparing them, as empirical rules, with the rule, equally empirical, which I propose to take their place. If I have been guilty of error, it is merely in applying the term "Method of L.S." to the rules rather than to the principles on which they are professedly founded. The only important question, namely whether the principles have any validity, these authors do not discuss; Dr. Stewart starts by assuming explicitly precisely those propositions which I am most concerned to deny.

Now, though this theorem is apparently accepted by all mathematicians who write on probability—for without it the theory of errors would not be mathematical at all,—no two of the most prominent exponents of the subject appear to agree exactly why it is true or exactly what it means. I do not propose to discuss it further here, but physicists, who are apt to accept “most probable” simply as synonymous with “most nearly right,” ought to be warned that the matter is not nearly as simple as it appears at first sight.

Experimental conceptions are introduced again in the premisses, whatever form they may take, which imply the Gaussian law of the distribution of errors. Of this law, no direct proof has been or can be offered. It is known that in many cases the distribution of the residuals is very near to the Gaussian and in no case widely different from it. But it is admitted that the residuals are not the errors; and what we actually know is always the residuals and not the errors. And it must be insisted once more that, by no possibility, can the true law be exactly Gaussian. Since all measuring instruments have a “step,” and since all observations have a least significant figure, the number of possible values within a given range is finite. The true law of distribution must be discontinuous, not continuous. That is an elementary fact which no amount of argument will alter; the Gaussian function can at best be the continuous series of points. But it is by no means certain that it is even this. The existence of the “decimal error” in subdividing a division is well known nowadays, and its distribution is not even approximately Gaussian. Further, the more nearly the “observations” represent real direct observations, unaltered by corrections or the taking of means, the more often (in my experience) is a deviation from the Gaussian distribution to be suspected. Example IV. is typical in this respect. The following table indicates that in the neighbourhood of zero error, the chance of an error does not decrease as rapidly with increase of its magnitude as the Gaussian law would predict; this feature is extremely frequent and is not unlikely on general grounds:—

Number of residuals between 0 and 9	Actual.	Calculated.
10 „ 19	10	15
20 „ 29	13	13
30 „ 39	15	10·5
40 „ 49	6	7
50 „ 59	7	4·5
60 „ 69	2	2
	1	1

For all these reasons it seems to me ridiculous to pretend that L.S. is so firmly established as the one and only correct method that no other is worth serious consideration, except perhaps as a mere approximation. According to the theory of error on which L.S. is based, Z.S. must approach asymptotically to it as the number of observations is increased. When that number is comparatively small, the minor departures from the premisses on which the theory is based are likely to be most serious; it is then that the question between Z.S. and L.S. really arises, and it is then that the unique validity of L.S. is most doubtful.

5. Again, even if it is admitted that L.S. must be in general somewhat nearer to the truth than Z.S., the question still remains whether the difference between the two is significant. Unless that question can be answered affirmatively, there will be no justification for the greater labour involved in L.S. Assuming the Gaussian theory, it might be possible, though extremely difficult, to calculate by how much the error of Z.S. in general exceeds that of L.S. But the result would tell us nothing about the relative merits of the methods, unless it could be shown that, in some possible experiment, the difference could be detected. And, if there is such an experiment, there is no need for argument; the matter will be settled in a manner beyond dispute.

Accordingly, it will be well to consider what kind of experiment might give the decision desired. If it can be found, it is sure to be exceedingly complicated and laborious, for the inquiry must necessarily be statistical: the Gaussian theory does not predict that L.S. gives always the true value, or always a value nearer the truth than any other method; it predicts only that in general the result will be nearer the truth. But the labour ought not to be shirked. The immense mathematical structure of the Gaussian theory rests on a very slight experimental foundation; a few superficial inquiries into the distribution of residuals is all the experimental evidence in its favour that is usually offered. It is time to divert attention from the elaboration of the superstructure to the strengthening of the foundations.

6. A decision would be possible if a and b were already known from some source of information independent of the observations. Such a condition is impossible to fulfil completely and satisfactorily; for reduction of observations by numerical computation is justifiable only when the observations themselves are as accurate as possible; if any known and avoidable source of error is present, it will almost always include some systematic error, which will not be

completely eliminated by any method of reduction. However, an approximation to the condition can be made. Suppose, for example, that we place a battery of E.M.F. E_0 in series with resistance R , an ammeter, a rheostat, and another source of potential, and read the current i flowing in the circuit together with the P.D. E between its ends. If r_1 and r_2 are the resistances of the battery and ammeter,

$$E = E_0 + i(R + r_1 + r_2), \dots \dots \dots (3)$$

which is of the form (1), if $a = E_0$ and $b = R + r_1 + r_2$. E_0 and the resistances can be measured independently by potentiometer and bridge methods of very great accuracy. The absolute values assigned to a and b will depend on the calibrations of the voltmeter and ammeter, which are subject to errors of the same order as those of the calculated a and b ; but if E_0 , R , are changed between successive experiments, the relative values are independent of calibration; further, if they are changed by reversals of the cells composing E_0 , and by the combination in series or parallel of the resistances composing R (r_1 and r_2 being small and known approximately), no absolute measures are necessary for the comparison.

This experiment has been carried out*, 15 comparisons being made. In 5 of them, the results of L.S. and Z.S. were practically indistinguishable. Of the remaining 10 cases, Z.S. was appreciably the more correct in 6, L.S. the more correct in 4. The comparison, if it displays any difference, is in favour of Z.S. It should be noted that, as the residuals showed, the errors were mainly "decimal," and therefore not distributed according to the Gaussian law.

A comparison of the same kind might be made in experiments directed to the determination of constants which are known theoretically. Thus observations by different methods of the value of h might be reduced by the two methods. The published results are not given in so much detail that the comparison can be made; and, even if they were, the strong probability that different methods are affected by different systematic errors would make the comparison uncertain.

7. Another possible method might be based on an examination of the maximum residual. Quite apart from any theory of errors, it is often possible to estimate, from the nature of the measurement and of the instruments with

* The experiments were made in 1914; the complete records have been lost, but a summary of them was recovered recently.

which it is made, the maximum error which can occur in taking an observation. If a reliable estimate of this maximum error can be made, and if any residual is found to exceed that error, then the value from which the residual is a difference cannot be the true value; the method of adjustment leading to that value must be false.

Such a method, if it could be applied, would be unexceptionable. But I have never succeeded in making any distinction between L.S. and Z.S. by means of it. Since authors (rightly) do not usually publish enough details of their experimental methods to enable the maximum error to be ascertained by others, I have been perforce confined to my own experiments, none of which have made any pretence to the highest accuracy. I have always found that, if only those experimental errors are taken into account which arise from the measuring instruments and can therefore be definitely foreseen, the maximum residual is always greater than the maximum error, whichever method of adjustment is adopted. If, on the other hand, allowance is made (as it doubtless should be) for failures to realize exactly the conditions intended, and for mere mistakes in reading or entry, the possibilities of error are so numerous and so vague as to lead to a maximum much greater than any residual. The method is commended to those whose experiments are better adapted to the purpose; but since the difference between the maximum residuals of L.S. and Z.S. is usually small, and not always in the same direction, the prospects of a decision by this method are not bright.

8. There is a third possible method less satisfactory theoretically than either of these, but easier to apply. It is familiar to all experimenters that the accuracy of a numerical result cannot be increased indefinitely (as it could be if the simple Gaussian theory of errors were true) by increasing the number of observations; the accuracy, for the purpose of this statement, is judged by the degree to which a repetition of the experiment leads to a repetition of the result. Suppose, then, that we make a number of determinations of the same a and b , each determination consisting of a considerable number of observations, reduce them both by L.S. and Z.S., and compare the degree of consistency given by the two methods of reductions. If one method of reduction gives notably better consistency than the other, there is some presumption in its favour. Such comparisons have been made, using measurements obtained in the calibration of Pirani pressure gauges; it should be noted that here there is known to be some slight systematic error, since the relation

involved is not perfectly linear. Four series of measurements were made on each of 7 gauges, each series consisting of from 22 to 26 observations. The maximum difference between two determinations for the same gauge, reduced by the same method, expressed as a fraction of the mean probable error was, for the 7 gauges

L.S. : 0.6, 1.4, 1.7, 1.3, 1.8, 0.7, 1.5.

Z.S. : 0.6, 1.6, 1.6, 1.1, 2.0, 0.9, 1.7.

The comparison this time is slightly in favour of L.S., but can hardly be regarded as more significant than the contrary result in the first test.

Such experimental tests of the efficiency of different methods of reducing observations are exceedingly tedious, and it is improbable that I shall have the opportunity of making many more of them. Anyone who is interested in the subject can easily continue them. In the meantime I would suggest that the onus of proof lies on those who would maintain that the superior accuracy of L.S. justifies the very great additional labour which it requires. Once more, it is useless to produce elaborate mathematical arguments to prove that L.S. in general gives the more correct value; if there is any physical significance in the statement that it is more correct, there must be some experimental test which will establish the statement; the only way to establish the statement is to make that test.

LXXIX. *Relative Probabilities of the Transitions involved in the Balmer Series Lines of Hydrogen.* By FRANK C. HOYT*.

I. *Introduction.*

ACCORDING to the quantum theory, the factors of fundamental importance for the processes of emission and absorption are the probabilities of transition in unit time from one stationary state of the atom to another, as introduced by Einstein in his deduction of Planck's law of temperature radiation. The correspondence principle of Bohr offers the possibility of connecting these probabilities with the properties of the motion of the atom, and thereby a basis for the estimation of the intensity of spectral line. In a previous paper† the general theory was briefly described,

* Communicated by Prof. N. Bohr.

† F. C. Hoyt, *Phil. Mag.* xlv. p. 135 (1923).

and some calculations of the relative intensities of X-ray lines were made on the basis of various plausible assumptions as to the exact relations between these probabilities and the motion; but as yet, however, there do not exist sufficient experimental data for a sharp distinction between these assumptions in this way. In the case of optical emission spectra, the number of atoms present in the initial states of the transitions involved in the emission of different lines is a factor which is very uncertain under the ordinary methods of excitation. This difficulty was avoided in the case of X-ray spectra, where the initial state is the same for a number of lines; but here the problem is greatly complicated by the complexity of the electronic motions. In optical absorption spectra we have to do, in many cases, with transitions from the same initial state of the atom, and it will be of particular interest to consider the lines of the Balmer series of hydrogen in this connexion, because here the motion may be completely treated on the basis of ordinary mechanics. To obtain direct absorption data of the necessary kind for these lines will perhaps present great difficulties; but, as pointed out by Ladenburg *, it may be possible to establish a connexion between the relative dispersion effects of spectral lines and the quantities which determine their relative absorption. In fact, Ladenburg and Reiche † have been able to obtain in this way an estimate, from dispersion data, of the relative probabilities of spontaneous transitions for H_α and H_β , which are in general agreement with the values indicated by a qualitative estimate based on the correspondence principle. It may therefore be of interest to make a comparison of the dispersion data with the values of these probabilities estimated on the various assumptions as to the quantitative application of the correspondence principle discussed in the previous paper.

II. Calculation of the Probabilities of Transition for the Components of the Balmer Lines of Hydrogen.

On the correspondence principle the probabilities of transition may be estimated by a comparison of the rate of emission of energy by a classical harmonic oscillator of frequency ν and amplitude Q with the quantity $h\nu A'_{mn}$, which represents this rate of emission on the quantum theory.

* R. Ladenburg, *Zeits. für Phys.* iv. p. 451 (1921).

† Ladenburg & Reiche, *Naturwissenschaften*, ix. p. 584 (1923).

This leads at once to the relation

$$A'_{nn} = \frac{1}{h\nu} \frac{32\pi^4 e^2}{3c^3} Q^2 \nu^4, \quad . \quad . \quad . \quad (1)$$

where A'_{nn} is the probability of spontaneous transition in unit time, and $Q^2 \nu^4$ may be considered as a kind of mean value of $C^2 \omega^4$, where ω and C are the frequency and amplitude of the corresponding harmonic component. For a multiply periodic system of degree of periodicity u , the frequency of the radiation emitted by a transition between two stationary states for which

$$\begin{aligned} I_r &= n_r' h \\ I_r &= n_r'' h \end{aligned} \quad (r=1, \dots, u)$$

respectively will, in fact, as pointed out by Kramers, be given by the formula

$$\nu = \int_0^1 \omega_\lambda d\lambda,$$

where λ is an auxiliary variable defining an intermediate state by the relation

$$I_r = I_r'' + \lambda(I_r' - I_r'').$$

The following six methods of evaluating the mean value were briefly discussed in the previous paper :—

$$Q^2 = \int_0^1 C_\lambda^2 d\lambda, \quad (A)$$

$$Q = \int_0^1 C_\lambda d\lambda, \quad (B)$$

$$\log Q = \int_0^1 \log C_\lambda d\lambda, \quad (C)$$

$$Q^2 \nu^4 = \int_0^1 C_\lambda^2 \omega_\lambda^4 d\lambda, \quad (D)$$

$$Q \nu^2 = \int_0^1 C_\lambda \omega_\lambda^2 d\lambda, \quad (E)$$

$$\log (Q \nu^2) = \int_0^1 \log (C_\lambda \omega_\lambda^2) d\lambda. \quad (F)$$

In the case of the hydrogen atom these quantities may be evaluated by graphical integration from the well-known expression for the harmonic representation of a rotating

ellipse, and in Table I. are given the relative values of A'' , for the fine-structure components of H_α and H_β , the two first lines of the Balmer series, the letters at the head of the columns corresponding to the six methods of averaging

TABLE I.
Relative Values of A'' .

Transition.	A.	B.	C.	D.	E.	F.
$\alpha_1 \ 3_3-2_2$	1	1	1	1	1	1
$\alpha_2 \ 3_2-2_1$	·451	·444	·432	·397	·414	·434
$\alpha_3 \ 3_1-2_2$	·0188	·0135	·00410	·00547	·00605	·000475
$\beta_1 \ 4_3-2_2$	·371	·316	·2371	·182	·169	·104
$\beta_2 \ 4_2-2_1$	·325	·303	·275	·354	·260	·172
$\beta_3 \ 4_1-2_2$	·0258	·0144	·00346	·00240	·00270	·00130

given above. From these values and the theoretical values of the statistical weights in the stationary states the probability coefficients B'' and B'' , for the forced transitions may be readily found from Einstein's relations,

$$B'' = \frac{g'}{g''} A'' \frac{c^3}{8\pi h\nu^3},$$

$$g'' B'' = g' B''.$$

Here g' and g'' are respectively the statistical weights of the stationary state of higher and lower energy. These weights are in the present case proportional to the subordinate quantum integers.

III. *Discussion of the Calculations.*

Unfortunately there exists at present. no fully adequate basis for a comparison of these calculated probabilities with experiment. From measurements on the absorption of the Balmer lines such a comparison might, however, be made in the following way. If N'' is the average number of atoms per unit volume present in the state of lower energy, the rate of absorption of energy is given by the expression

$$\rho_\nu N'' B'' h\nu,$$

where ρ_ν is the density of radiation of frequency ν . We

thus have for the average coefficient of absorption σ for a given line

$$\sigma = N'' B'' h\nu,$$

or, making use of Einstein's relation,

$$\sigma = N'' \frac{g'}{g''} A'' \frac{c^3}{8\pi\nu^2}.$$

In Table II. are given the relative values of σ for the fine-structure components of H_α and H_β computed from eq. (2) and from the values of A'' in Table I. Now, in any ordinary experiment the components would hardly be separated, and it will be necessary to estimate the total absorption of the

TABLE II.

Relative Values of $\sigma/N'' = \frac{g'}{g''} A'' \frac{c^3}{8\pi\nu^2}$.

Transition.	A.	B.	C.	D.	E.	F.
$\alpha_1 \ 3_3-2_2$	1	1	1	1	1	1
$\alpha_2 \ 3_2-2_1$	·600	·592	·576	·529	·552	·579
$\alpha_3 \ 3_1-2_2$	·00627	·00449	·00137	·00182	·00202	·000158
$\beta_1 \ 4_3-2_2$	·151	·129	·0963	·0741	·0686	·0421
$\beta_2 \ 4_2-2_1$	·176	·164	·149	·192	·141	·0934
$\beta_3 \ 4_1-2_2$	·00350	·00195	·000469	·000325	·000364	·000176
$\sigma_\alpha = \frac{2a_1 + a_2 + 2a_3}{2\beta_1 + \beta_2 + 2\beta_3}$	5·39	6·12	7·53	7·44	9·17	14·5

three components of each line. Here we must take into account the relative number of atoms present in the different initial states. Under conditions of thermal equilibrium we should have

$$N'' = \text{const.} \times g'' e^{-\epsilon''/kT},$$

where ϵ'' is the energy and T the temperature. At sufficiently high temperatures the values of N'' would thus be proportional to g'' since the differences in energy are small, and there would be twice as many atoms in the 2_2 states as in the 2_1 states, the statistical weights, as above mentioned, being in this case proportional to the subordinate quantum integers. The values of the ratio $\sigma_\alpha/\sigma_\beta$ given in the last row

are calculated on this assumption. It may, however, be emphasized that if the excitation is not produced by thermal equilibrium but, for instance, by electron bombardment, the ratio of the number of atoms in the 2_1 and 2_2 states may be very different from that used in the calculation.

The relative values of σ could be found from measurements of the total absorption and compared with the values calculated by eq. (2), but such data do not exist for these hydrogen lines, and to obtain them might involve very great difficulties. However, as suggested by Ladenburg, the relative values of σ may be obtainable from measurements on anomalous dispersion. In fact, according to the classical theory as ordinarily interpreted, the quantity σ is given by the expression $N \frac{\pi e^2}{m}$, and the same expression

occurs in the classical dispersion formula. Ladenburg has therefore, in the paper mentioned in the Introduction, taken the view that the probabilities of transitions between stationary states, which on the quantum theory are responsible for the absorption, may be obtained from the course of the dispersion curve in the neighbourhood of the absorption line. In this way he has, from his measurements on the dispersion of H_α and H_β in luminous hydrogen, arrived at the value 4.5 for the relative absorption coefficient $\sigma_\alpha/\sigma_\beta$ as a mean of values lying between 3 and 6.

The results in this table are seen to differ greatly for the different methods of averaging used, and dispersion data might therefore be of importance for an eventual choice between these methods. At present, however, the experimental data are hardly of sufficient accuracy to allow a definite choice. In this connexion it may be remembered that the experiments among other uncertainties involve a fundamental one on account of the fact that the measurements of the dispersion are made under a heavy electric discharge. As pointed out by Ladenburg, this discharge may have a considerable influence on the structure of the lines due to the perturbations of the electronic orbits. It may also considerably affect the ratio between the number of atoms present in the initial states.

The author wishes to express his thanks to Professor N. Bohr for his kind interest in the preparation of his paper.

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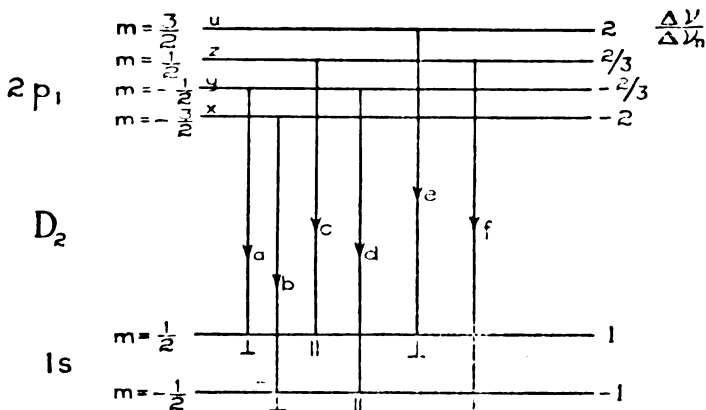
LXXX. *The Polarization of Resonance Radiation.* By G. BREIT, *National Research Fellow, The University of Minnesota* *.

EXPERIMENTS on the polarization of resonance radiation in a magnetic field have been described by Wood and Ellett †, and the Zeeman effect in resonance radiation has been discussed theoretically by Foote, Ruark, and Mohler ‡. I should like to point out that the Zeeman effect discussed in accordance with the Landé-Sommerfeld-Heisenberg theory in the manner of Foote, Ruark, and Mohler accounts for the magnitude of polarization observed in sodium vapour, and to accentuate the difference in the observed behaviour of sodium and mercury in an external field.

1. Polarization in Strong Fields.

We first discuss the effects in a magnetic field of sufficient strength (100 gauss) to make the state of polarization depend mainly on the field. Sodium will be used as an example, since the data are more complete for this element. The

Fig. 1.



Zeeman patterns of D_2 and D_1 are due to transitions between levels drawn in figs. 1 and 2. The arrows indicate transitions and the signs $\parallel$ or $\perp$ indicate that the component is polarized parallel or perpendicular to the applied field. We take D_2

* Communicated by the Author.

† Proc. Roy. Soc. A, ciii, p. 396 (1923).

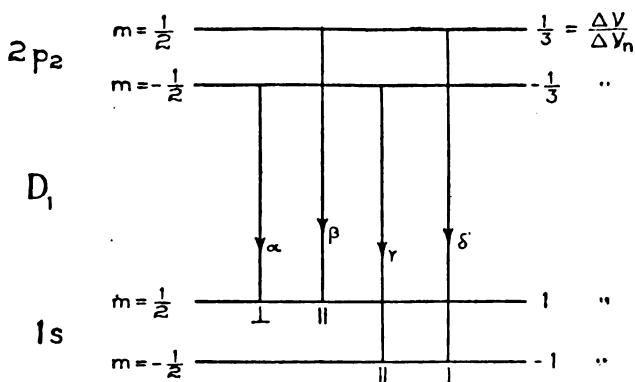
‡ Journal of the Optical Society of America, vii, p. 415 (1923).

to be twice as strong as D_1 and the relative intensities of the Zeeman components to be as given by Paschen and Götze in *Seriengesetze der Linienspektren* (Berlin: Julius Springer, 1922), p. 154, so that

$$\frac{a}{8.8} = \frac{b}{14.6} = \frac{c}{14.6} = \frac{\alpha}{10} = \frac{\beta}{9} \dots \dots \dots (I)$$

If the intensities of the Zeeman components had been measured in a tube-furnace with a small outlet, the statistical populations of all the $2p_1$ levels would be the same to a good approximation. The same is true for the levels of $2p_2$. The numbers given in (1) will measure, therefore, actual probabilities of transitions.

Fig. 2.



To obtain the relative intensities of the Zeeman components in resonance radiation, we need some conceptions introduced by Einstein * in his derivation of Planck's radiation formula. Let E_m and E_n be the energies of a gas molecule in two quantized states m and n respectively. Let m be greater than n . If the molecule is in the state m , there is a probability $A_m^n dt$ that in the time dt it will pass spontaneously to n with emission of radiation. A_m^n is a constant for a given combination of indices.

If the molecule is surrounded by radiation passing in random directions the volume density of which is $\rho(\nu)d\nu$ for the frequency range $\nu, \nu + d\nu$, the probability, due to ρ , of a change of state from n to m per second is written by Einstein as $B_m^n \rho$, and the probability of a change from m to n is similarly written as $B_m^m \rho$. If the *a priori* probabilities of n and m are

* *Phys. Zeit.* xviii. p. 121 (1917).

p_n , p_m respectively, Einstein showed that

$$p_n B_n^m = p_m B_m^n,$$

and that

$$\frac{A_m^n}{B_m^n} = \alpha \nu^3,$$

where α is a universal constant.

Therefore if $\frac{p_n}{p_m}$ is kept constant, $\frac{A_m^n}{B_m^n}$ is also unchanged.

This fact is fundamental in the derivation below.

Under the experimental conditions used by Wood and Ellett the pressure is so low that the excitations of D_1 and D_2 are separate *, and the incident radiation is so weak that the amount of resonance radiation is proportional to the incident energy.

The above considerations apply to black-body radiations reacting with an atom of the simplest type, and do not take into account the influence of polarization. A slight modification of the above concepts must be made if polarization is considered.

In a magnetic field the emission occurs in quanta, some of which are linearly and some circularly polarized. The directions of linear polarization and of the axes of circular polarization are parallel to the magnetic field.

Let us consider the case of a linearly-polarized component. Let the incident wave be plane and linearly polarized in such a way that the angle between the electric intensity of the incident wave and the applied magnetic field is θ . Experiments on the inverse Zeeman effect (and the classical theory of the Zeeman effect) indicate that the probability of absorbing a quantum from the wave is proportional to $\cos^2 \theta$.

In the case of circularly-polarized components conditions are very similar to those of linear polarization, the only difference being that the "radiation" emitted is circularly polarized. According to the Principle of Correspondence, the probability of the absorption of a linearly-polarized wave by a circularly-polarized component must be related to the probability of the absorption of a circularly-polarized wave by the same component in a manner similar to that in which the component would absorb on the classical theory. For equal energies, therefore, a wave linearly polarized with the electric vector perpendicular to the magnetic field gives a

* Wood, 'Researches in Physical Optics,' pt. ii. p. 174 (Columbia University Press, 1919).

probability of absorption of a quantum which is only one-half of what it would be if the wave were circularly polarized. More generally if the wave normal P and the electric vector E be chosen as a system of polar coordinates θ, ϕ (θ = complement of latitude measured from E ; ϕ = longitude measured from P in a plane perpendicular to E) to which we refer the magnetic field H , then the circular vibration "corresponding" to the circularly-polarized Zeeman component may be broken up into two equally intense linear components at right angles to each other and 90° out of phase. For the directions of resolution we choose $(\frac{\pi}{2} + \theta, \phi)$ and $(\frac{\pi}{2}, \phi + \frac{\pi}{2})$. The second of these is not affected by E , being at right angles to it. The first, when resolved along E , becomes multiplied by $\sin \theta$. Since its intensity is one-half of the intensity of the circular vibration, the probability of absorption is $\frac{1}{2} \sin^2 \theta$ on the same scale as that in which the probability of absorption of a quantum from a linearly-polarized wave is $\cos^2 \theta$ if θ is the angle between the directions of polarization of the wave and of the linear Zeeman component (H). Before passing on to the numerical calculations involving (I), we must consider the meaning of (I) in more detail.

The numbers $a, b, c, \dots$ refer to intensities observed in a direction perpendicular to the applied magnetic field. The components c, β, d, γ are linear and the remaining ones are circular. It is clear that the total energy sent out in the form of the circular components is underestimated by a factor of 2 on account of the inefficient angle at which these components are observed in comparison with the linear components. The probabilities of transitions are therefore proportional to

$$2a, 2b, c, 2\alpha, \beta \dots \dots \dots (I')$$

for equal times of remaining in the excited levels.

If the atom has been excited to the level x (fig. 1), the probability of returning to the lower energy state is 1 during any appreciable time. Thus the probability of the emission of the component (b) is simply proportional to the probability of the excitation of x . This level is excited by absorbing b when the atom is in the lower of the two equally probable (1s) levels. Letting θ be (as before) the angle between the electric intensity of the incident wave and the applied magnetic intensity, the probability of the absorption of b is $2b \frac{\sin^2 \theta}{2} = b \sin^2 \theta$, and this, therefore, is also the probability

of its re-emission. On the light-quantum theory the lateral emission of b has then a probability equal to that of the re-emission of b .

If the atom has been excited to the level (y), it may return to ($1s$) along a or d . The probabilities of these two returns are to each other as $2a$ is to c (since d, c are symmetrical), and since the total probability of a return is certainty, these two probabilities are $\frac{2a}{2a+c}$ and $\frac{c}{2a+c}$. Just as in the case of b , the probability of absorbing a is $a \sin^2 \theta$ and that of absorbing c is $c \cos^2 \theta$, the total probability of reaching y being therefore $a \sin^2 \theta + c \cos^2 \theta$, and the probabilities of radiating a and c are

$$\frac{2a}{2a+c} (a \sin^2 \theta + c \cos^2 \theta)$$

and

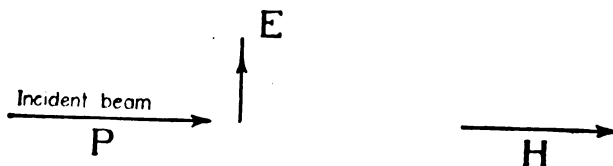
$$\frac{c}{2a+c} (a \sin^2 \theta + c \cos^2 \theta).$$

Similarly for α and β these quantities are $\alpha \sin^2 \theta$, $\beta \cos^2 \theta$,

$$\frac{2\alpha}{2\alpha+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta),$$

$$\frac{\beta}{2\alpha+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta).$$

Fig. 3.



Let the line of sight be perpendicular to the plane of the paper in fig. 3, H remaining in the direction θ, ϕ . We shall need in what follows the relative proportions of light polarized along E and along P . The linear components contribute:

$$\cos^2 \theta \text{ along } E$$

and

$$\sin^2 \theta \cos^2 \phi \text{ along } P.$$

The circular Zeeman components may be first broken up into two equal parts along $\left(\frac{\pi}{2} + \theta, \phi\right)$ and $\left(\frac{\pi}{2}, \phi + \frac{\pi}{2}\right)$, the

intensity of each being $\frac{1}{2}$ of the intensity of the whole. The first of these gives $\frac{1}{2} \sin^2 \theta$ along E and $\frac{1}{2} \cos^2 \theta \cos^2 \phi$ along P. The second gives 0 along E and $\frac{1}{2} \sin^2 \phi$ along P, giving for both (since their phase-difference is $\frac{\pi}{2}$) $\frac{1}{2} \sin^2 \theta$ along E and $\frac{1}{2} (\sin^2 \phi + \cos^2 \theta \cos^2 \phi)$ along P. The two amounts are therefore :

$$\begin{aligned}
 E &= \left[\frac{2a}{2a+c} (a \sin^2 \theta + c \cos^2 \theta) + \frac{2\alpha}{2\alpha+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta) \right. \\
 &\quad \left. + b \sin^2 \theta \right] \frac{\sin^2 \theta}{2} + \left[\frac{c}{2a+c} (a \sin^2 \theta + c \cos^2 \theta) \right. \\
 &\quad \left. + \frac{\beta}{2\alpha+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta) \right] \cos^2 \theta, \\
 P &= \left[\frac{2a}{2a+c} (a \sin^2 \theta + c \cos^2 \theta) + \frac{2\alpha}{2\alpha+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta) \right. \\
 &\quad \left. + b \sin^2 \theta \right] \cdot \frac{1}{2} (\sin^2 \phi + \cos^2 \theta \cos^2 \phi) \\
 &\quad + \left[\frac{c}{2a+c} (a \sin^2 \theta + c \cos^2 \theta) + \frac{\beta}{2\alpha+\beta} (\alpha \sin^2 \theta \right. \\
 &\quad \left. + \beta \cos^2 \theta) \right] \sin^2 \theta \cos^2 \phi.
 \end{aligned}$$

Case I. Let E, P, H be as in fig. 3, the line of sight being perpendicular to the plane of the figure. We want to know the state of polarization. We have $\theta = \frac{\pi}{2}$, $\phi = 0$. From the expressions for E and P it follows that

$$\frac{E-P}{E+P} = \frac{\frac{b}{2} - \frac{a(c-a)}{2a+c} - \frac{\alpha(\beta-\alpha)}{2\alpha+\beta}}{\frac{b}{2} + \frac{a(c+a)}{2a+c} + \frac{\alpha(\beta+\alpha)}{2\alpha+\beta}} = 0.30.$$

Wood and Ellett record 30 per cent. polarization.

Case II. Let E, P be as in Case I., but let H be parallel to E in fig. 3. Using the values of E and P and letting $\theta=0$, we have

$$\frac{E-P}{E+P} = \frac{\frac{c(c-a)}{2a+c} + \frac{\beta(\beta-\alpha)}{2\alpha+\beta}}{\frac{c(c+a)}{2a+c} + \frac{\beta(\beta+\alpha)}{2\alpha+\beta}} = 0.14.$$

It appears from the article of Wood and Ellett that the

polarization in this case was not much weaker than in Case I. It thus appears that the theory of light quanta gives a too small value for the polarization. However, no definite statement as to the amount of polarization is made by Wood and Ellett.

Case III. Wood and Ellett observed that if H is in the plane of E and P, and if $\theta = 45^\circ$, the polarization disappears. There is no polarization if the intensities of the circular components are equal to the intensities of linear components. This means :

$$\tan^2 \theta = \frac{\frac{c(c-a)}{2a+c} + \frac{\beta(\beta-a)}{2a+\beta}}{\frac{b}{2} - \frac{a(c-a)}{2a+c} - \frac{\alpha(\beta-a)}{2a+\beta}}, \quad \theta = 31^\circ.$$

This differs from 45° by an amount greater than can be accounted for by experimental error. The discrepancy indicates perhaps the presence of influences enhancing C, B at the expense of other components. The handing-on of radiation may be suspected as such an influence.

Case IV. Let E be perpendicular to the plane of the paper in fig. 3, and H have the direction shown in the figure. The vapour is sensitive to the circular components only, and thus the case is not different from I.

Case V. Let E be as in IV., and H parallel to the position of E in fig. 3. Again only the circular excitation takes place. Hence the same result as in I.

Case VI. Positions of H intermediate between IV. and V. give the same result; the direction of polarization simply rotates with the field.

The behaviour deduced in IV., V., VI. is the observed behaviour. The observations on mercury in a field of reasonable strength appear to fit into the same scheme. Of course, all disturbing influences (collisions, secondary resonance radiation, light scattered by the walls of the bulb) will cause depolarization.

2. Polarization in Sodium in a Weak Field or in the absence of an External Field.

Let the magnetic field have no definite orientation, and let all directions of the field be equally probable. Suppose also that the variations in the field are slow in comparison with the time of excitation. Then the resultant polarization can be obtained by averaging the expressions for E and P.

We obtain

$$\frac{E-P}{E+P} = \frac{\frac{2(a-c)^2}{2a+c} + \frac{2(a-\beta)^2}{2\alpha+\beta} + b}{7(a+\alpha+b) + 3(c+\beta) + \frac{c(c-a)}{2a+c} + \frac{\beta(\beta-\alpha)}{2\alpha+\beta}} = 0.055.$$

Wood and Ellett (*l. c.*) observed 5 per cent. polarization in the absence of a magnetic field for sodium.

We have supposed in the above calculation that the magnetic field does not change its direction during a time long enough to allow the atom to absorb the incident radiation and then to re-emit it again. This supposition is, of course, itself questionable, and its validity depends upon experimental conditions. It is difficult to suppose that the magnetic field is of an intermolecular nature because the time during which two atoms are likely to be sufficiently close to each other to act with a field of 100 gauss is likely to be only 10^{-11} sec, whereas the time of excitation is of the order of 10^{-8} sec.

On the other hand, if the magnetic field during emission should have a random distribution of directions with respect to the field during absorption, and if the atom should be affected by both fields in its quantization, then the radiation must be entirely unpolarized.

3. Polarization of Mercury Vapour in the absence of a Magnetic Field.

If considerations similar to those applied to sodium should be carried through for mercury, similar results would be obtained, whereas Wood and Ellett find 90 per cent. polarization in the absence of a magnetic field. This result is very puzzling inasmuch as it seems to imply that the incident wave has orienting influence on the "corresponding" radiating mechanism. If this "corresponding" mechanism is linear, the axis of vibration is to be thought of as directed along the electric vector of the incident wave. If the mechanism is circular, the plane of vibration is to be thought of as perpendicular to the wave normal. A differentiation between the two mechanisms could be obtained by examining the radiation in directions oblique to the incident beam. Such observations, however, are not available.

The possibility of simultaneous actions by two atoms in this case cannot be postulated unless it is also supposed to be fundamental when the magnetic field is present, for otherwise the intensities observed with and without the field would be different.

It must be remarked, however, that the application of the Principle of Correspondence in the above discussion is only tentative. Thus one cannot deny the possibility of a correspondence between the whole phenomenon of resonance radiation: (a) on the classical theory, (b) on the theory of quantized levels. If, then, the Hg atom should correspond to a classical linear resonator performing a forced oscillation, complete polarization would result.

We see from the amounts of polarization recorded by Wood and Ellet that the quantization of Hg in a magnetic field does not appear to hold when H is less than 2 gauss. (In sodium a field of the order of 100 gauss was required.) Without attempting to see what happens for these small fields, one can suppose that their magnitude is such that the Larmor precession* has a period which is too long in comparison with the average time τ during which the mercury atom remains in the excited state. In a field of two gauss the Larmor precession has a period of roughly 3×10^{-7} sec.; the assumption is that the quantization is diffuse if the atom returns to the normal state in a time comparable with the period of this precession—that is, the quantum conditions cannot be applied to a coordinate unless that coordinate *actually passes* through changes of a periodic character.

The experiments of Franck and Cario† and of Cario‡ support the view that, if all the collisions are effective in removing energy from excited Hg atoms, the time τ is of the order 10^{-8} sec. Wood§, however, gives $\frac{1}{15800}$ sec. as the time required for the appearance of the green fluorescent radiation when mercury vapour is illuminated at a pressure of 2.5 mm. This is the time between two collisions bringing about fluorescence. Taking the mean free path at 760 mm. pressure as 1.6×10^{-5} cm. and the mean velocity as 1.7×10^4 cm./sec., the interval between collisions at 2.5 mm. is roughly 3×10^{-7} sec., while Wood obtains 6×10^{-5} sec. One might suppose, therefore, that collisions bringing about fluorescence are 100 times more rare than ordinary collisions. If this result may be extended to the case of Hg resonance radiation, and if the pressure-effects discussed by Cario and by Cario and Franck are to be left unchanged, their time τ must be multiplied by about 100; the resulting value is of the order of magnitude of the Larmor precession for two

* See *Atombau*, 3rd ed., p. 364.

† *Zs. f. Phys.* xi. p. 161 (1922).

‡ *Zs. f. Phys.* x. p. 185 (1922).

§ *Proc. Roy. Soc. A*, xcix. p. 362 (1921).

gauss. Wood * has described experiments in which secondary resonance radiation in Hg was photographed with a quartz plate inserted at the edge of the primary beam. Under these conditions no excited molecules from the primary beam can travel into the region of the secondary radiation, and the entire secondary effect is due to radiation which has passed through the quartz plate. On comparing the photograph with one taken in the absence of the quartz plate, it was found that the decrease in intensity of the secondary radiation was about 25 per cent., while loss by reflexion at the plate is about 10 per cent. Thus it is probable that a portion of the secondary radiation is due to atoms which travel out of the path of the primary beam, and by measuring the width of the secondary strip an estimate of the time τ can be obtained. Wood's value is about 10^{-5} sec. This result has been questioned by Stern † on the basis that the reflexion power of the quartz may have been underestimated. So far as we know, the question is still unsettled, but the probability is that the time τ is actually considerably larger than 10^{-8} sec.

For Na, the classical estimate of $\tau = 10^{-8}$ sec. is in agreement with the order of magnitude of the period of the Larmor precession for 100 gauss, which is the field used by Wood and Ellett ‡. This suggests that the difference in τ of Hg and Na is due to the fact that $\lambda 2536$ of Hg is a combination line and that classical estimates are not applied to it as readily as to ordinary lines. The behaviour of Hg in a magnetic field observed by Franck and Grotrian § shows that something not considered in the above discussion is brought about by the magnetic field; of course, the experiment of Franck and Grotrian had reference to the fluorescent molecular radiation.

* *Phys. Zeit.* xiv. p. 177 (1913). The author's attention has been called to these experiments and their criticism by Stern, by Mr. A. E. Ruark.

† *Phys. Zeit.* xx. p. 183 (1919).

‡ It must be pointed out that the behaviour of D_1 and D_2 for separate excitation observed by Wood and Mohler (*Phys. Rev.*, n.s., xi. p. 70, 1918) points toward a larger value for τ , say 5×10^{-6} sec. For the small energy transfer between D_1 and D_2 it may be that the atoms are to be considered as colliding even when at a considerable distance apart. A factor of ten in the radius causes a factor of 100 in the mean free path and in the collision interval. Stern (*l. c.*) has pointed out that excited atoms have larger diameters than normal ones, and that this must be taken into account in estimates of collision intervals. Cario has utilized this fact in his estimates of τ (*l. c.*).

§ *Zs. f. Phys.* vi. p. 35 (1921).

Summary.

A quantitative elaboration of the consequences of the Zeeman effect in resonance radiation gives polarizations in fair agreement with observed values of Wood and Ellett, for sodium in a strong magnetic field and in the absence of a field.

The value of H which suffices to establish the space quantizing appropriate to a magnetic field is tentatively brought into connexion with the period of the Larmor precession as compared with the time constant τ of the atom. Numerical agreement is attained in the case of mercury if $\tau \cong 10^{-6}$ sec. rather than 10^{-8} sec. Evidence in favour of $\tau \cong 10^{-6}$ sec. is adduced; it is suggested that not all collisions are effective in causing fluorescent emission; since this also explains the measurements of Wood on the time lag of fluorescence in mercury vapour. The case of sodium is treated on the assumption that $\tau \cong 10^{-8}$ sec.

Mr. A. E. Ruark, of the Johns Hopkins University and of the National Bureau of Standards, is responsible for the thought that the Zeeman effect may account for the polarization of resonance radiation. He has also contributed most generously to the improvement of every part of this paper, having checked through the calculations and gone over the experimental evidence. The writer's sincerest thanks are due to him for this assistance.

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LXXXI. *The Charging Effect produced by the Rotation of a Prolate Iron Spheroid in a Uniform Magnetic Field.* By
ERNEST LAWRENCE, M.A.*

Introduction.

PROFESSOR W. F. G. SWANN† has discussed the interpretation of the "Moving-Line Theory" of electromagnetic induction which is consistent with Maxwellian theory for the case of a symmetrically magnetized system rotating about the axis of symmetry. At a subsequent time he carried out an experiment confirming these conclusions

* Communicated by Prof. W. F. G. Swann.

† Swann, Phys. Rev. (2) xv. pp. 365-398 (1920); Phys. Rev. (2) xix. p. 381 (1922).

for the case of a rotating magnetized sphere. For reasons which will appear later it was deemed worth while to repeat the experiment for a prolate spheroid rotating and magnetized symmetrically about its major axis. The theoretical formulæ for an ellipsoid were worked out by Dr. Rognley*, of this department, and the present experiment forms a verification of his results.

Theoretical Considerations.

The theory immediately involved in the experiment may be briefly summarized as follows:—

The force acting on an electron is

$$\text{where } \mathbf{F} = \mathbf{E} + \frac{[\mathbf{V}\mathbf{H}]}{C}$$

$$\mathbf{E} = -1/C \frac{\partial \bar{U}}{\partial t} - \text{Grad } \phi,$$

$\bar{U}$ and ϕ being the usual vector and scalar potentials, respectively, while $\mathbf{E}$ and $\mathbf{H}$ are the electric and magnetic

vectors. For the case of a rotating spheroid $\frac{\partial U}{\partial t}$ is zero by

symmetry so that $\mathbf{E}$ is derivable from a potential. It is found that the scalar potential ϕ is of the type resulting from an electrostatic polarization giving rise to a fictitious volume and surface distribution of electricity. It follows,

neglecting the so-called "Motional Intensity" $\frac{[\mathbf{V}\mathbf{H}]}{C}$, that

the electrons in the magnet will redistribute themselves so that the electric field at all points will be zero. The "Motional Intensity" will cause a further rearrangement of the electrons which will in general alter the potential of internal and external points. In this manner the potential of the axis of the spheroid is altered by rotation, so that when the axis is earthed a charge comes to the ellipsoid. The potential of a metal shell surrounding the rotating system would be altered as a result of the appearance of such a charge, resulting in the movement of the spot of an attached electrometer system. Dr. Rognley showed this alteration of potential to be:

$$\Delta V = - \frac{4\pi n B b^2}{3C} q_{12}/q_{22}, \quad . \quad . \quad . \quad (1)$$

where B is the total magnetic induction in the spheroid, b the minor axis, and the q 's are the usual coefficients of

* Rognley, Phys. Rev. (2) xix. p. 609 (1922).

capacity and induction, the subscripts 1 and 2 referring to the spheroid and shell (with attached electrometer system), respectively. n is the number of revolutions per second and C is the velocity of light.

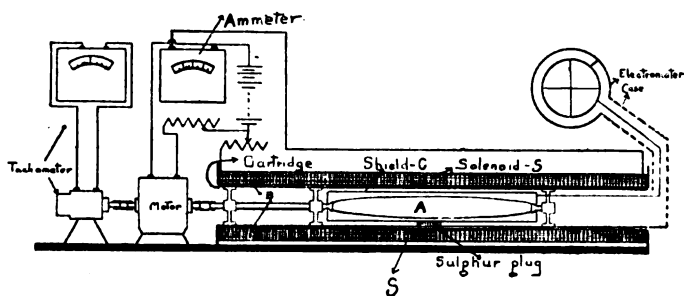
It is of interest to here note that B is the total magnetic induction in the iron. Dividing the induction into two parts, one associated with the magnetization of the spheroid and the other with the external field, a plausible but erroneous view would be one in which the lines of the former field rotated with the spheroid and produced no electrical effects, while the lines of the latter field produced the full effect calculated from (1)—with B replaced by the external field. For the ellipsoid used, such a view leads to a value for ΔV of the order of magnitude of three per cent. of the value given by the correct theory referred to above. The experiment on the rotation of a sphere provided a conclusive test of the theory, but there the difference between the conclusions of the correct and the erroneous theory amounted to a factor of only three while in the case of the rotation of a prolate spheroid the difference amounts to a factor of thirty. The experiment has a further interest in that it is a representative of a class of experiments which have been performed before but in which such effects as might have been obtained were screened off on account of the particular arrangement of apparatus used.

Experimental Procedure.

Fig. 1 indicates the details of the apparatus. An ellipsoid A of mild steel having minor axis two centimetres and major axis twenty centimetres was mounted on brass shafting, the shafting being soldered to the extremities of the ellipsoid. Bearings for the shafting were mounted in a brass tube B having a removable cover; and ellipsoid and shaft were mounted therein, in such a manner as to be readily accessible through the cover. A shell C , cylindrical in shape, was mounted on sulphur, so as to surround the ellipsoid in the tube. It was so designed as to be readily opened for access to the ellipsoid. The tube assembly thus described will henceforth be referred to as the "cartridge." A solenoid S , of such dimensions as to produce a uniform saturation magnetomotive force over the ellipsoid, when the cartridge was inserted therein, was made by winding number 10 copper wire on a brass tube slightly larger than the cartridge tube. The cartridge was inserted in the solenoid and the shaft connected to a high-speed motor which also was connected to a Hopkins Electric Tachometer. The quadrant of a

Dolezalek electrometer was connected directly to the shell in the cartridge, the cartridge tube, bearings, etc., being connected to the case of the electrometer system. Suitable rheostats provided means of regulating the speed of the motor and the current flow in the solenoid. A ballistic galvanometer calibrated by a Hibbert Standard was used in the determination of fluxes in the ellipsoid.

Fig. 1.



The ellipsoid was set in rotation, and the speed adjusted by a rheostat to the value desired. At the same time the current in the solenoid was adjusted to a definite value and the motion of the electrometer spot was watched. The tachometer dial and ammeter were so placed as to enable the experimenter to keep close check on all three readings simultaneously. The current and speed were adjusted continually and the moment it was evident that the electrometer spot was steady and the current and speed had the desired values, the position of the spot was noted. Then, immediately, the current in the solenoid was reversed by the throw of a commutator switch, and again the operation of adjusting current, speed, etc., was carried out and the reading of the deflected spot was taken. A second reversal of current with a like process of observation brought the spot back to approximately the first reading. This set of operations was repeated three to five times, according as the readings were deemed reliable. Next the current was changed to another value and the above procedure repeated. Measurements were made in this manner for four different currents, and with four different speeds of rotation for each value of the current.

It was found that there existed at intervals a drift of the electrometer needle which was attributed to thermocouple effects in the solenoid interior, as it was noted that the rate

of drift increased with the temperature of the solenoid interior. This fact, incidentally, made it necessary to take the cartridge out after each run of observations and cool it in order that the drift should be kept at a minimum.

The ratio q_{12}/q_{22} was determined as follows: The ellipsoid was insulated in its bearings by paper. The shell-electrometer system was insulated with the ellipsoid earthed, and the latter was then raised to a potential V_1 . The shell rose in consequence to a potential V_2 which, since the shell and electrometer were both insulated, is related to V_1 by

$$q_{12}V_1 + q_{22}V_2 = 0.$$

Thus, it is only necessary to know V_1 and V_2 in order that the q ratio be known. If θ_1 is the electrometer deflexion corresponding to the potential V_1 and θ_2 the deflexion which results from applying a potential V_2 to the quadrant, it follows that

$$\frac{\theta_1}{\theta_2} = \frac{V_1}{V_2} = -q_{22}/q_{12},$$

which serves to determine q_{12}/q_{22} .

The mean of four determinations gave $q_{12}/q_{22} = -0.235$.

The electrometer sensitivity was determined in the usual manner, namely, by applying a known potential and noting the deflexion resulting therefrom. Determinations of the sensitivity taken throughout the range of the scale involved in the experiment showed that variation from proportionality of potential and deflexion was negligible.

The determination of the fluxes through the ellipsoid corresponding to the various currents in the solenoid presented difficulties requiring close attention. The ballistic galvanometer was mounted at a sufficient distance from the solenoid to ensure that stray fluxes produced errors of less than one per cent. Since the magnetic induction B is determined by dividing the total number of maxwells cut by the total area of the turns of wire wound on the ellipsoid enclosing the flux, it was necessary to ascertain the cross-sectional area of the ellipsoid at the point with considerable care, as an error of 0.5 millimetre in the measurement of the radius of the circular cross-section of the ellipsoid enclosed by the wire corresponded to an error of 5 per cent. in the final result. The galvanometer was calibrated from the throws of a Hibbert Standard Coil, which had itself been previously calibrated to within a tenth of one per cent.

Results.

A complete tabulation of data and results obtained is of little importance and too lengthy to print, and it will suffice to give a resumé of the final results embodied in the following table.

No. of Observations.	Speed R.P.M.	B E.M.U.	Volts ($\times 10^{-2}$) Observed.	Volts ($\times 10^{-2}$) Calculated.	Difference per cent.
4	2400	14,900	2.37	2.37	0.0
4		16,500	2.69	2.64	+1.9
4		19,100	3.09	3.04	+1.6
3	3200	14,900	3.19	3.18	+0.3
4		16,550	3.54	3.52	+0.5
4		17,950	3.78	3.82	-1.0
3		19,100	4.03	4.06	-0.7
4	4000	16,550	4.55	4.40	+3.4
5		17,950	4.87	4.77	+2.0
5	4800	17,950	5.74	5.72	+0.4
3		19,100	6.04	6.10	-1.0

The first column numbers indicate the number of observations for the particular set of conditions of speed and magnetic induction indicated in the second and third columns for which the change in potential of the fourth column represents the mean. The fifth column gives the theoretical value for the change in potential which is the object of verification.

The average discrepancy between the calculated and observed values estimated regardless of sign is 1.2 per cent. while the greatest deviation is 3.4 per cent. In view of the smallness of the quantities measured and the exceptional conditions attendant with high rotational velocities and large magnetic fluxes, the results as set forth may be considered a satisfactory experimental confirmation of the theoretical formula.

The writer wishes to take this opportunity to express his sincere thanks to Prof. W. F. G. Swann, who assigned the problem, for his continued interest and advice. He wishes also to express appreciation of the services of Mr. C. Dane, the laboratory mechanic, and Mr. W. B. Haliday, who aided in setting up the apparatus.

Department of Physics,
University of Minnesota.
Sept. 29, 1923.

LXXXII. *The Anhyseretic Qualities of Iron and Nickel and the Energy Change at the Critical Temperature.* By J. R. ASHWORTH, D.Sc.*

INDEX TO PARAGRAPHS.

1. Development of an equation to anhyseretic curves of $I = \phi(H)$.
2. Experiments to trace anhyseretic isothermals.
3. Results obtained with iron and the determination of R_1 and its relation to R' .
4. Determination of the ferromagnetic field Constant a_1 ; Relation of R' , a' and R_1 , a_1 .
5. Results obtained with nickel and the values of R_1 and a_1 .
6. Corresponding states for $I = \phi(H)$.
7. Relation of R_1 to I_0 .
8. Energy change in passing from ferromagnetism to paramagnetism
9. Table of constants and equations.

1. **A** FERROMAGNETIC substance above its critical temperature behaves as a paramagnetic body and obeys the simple law expressed by the equation

$$\frac{H}{I} = R'T, \quad (1)$$

where H is the applied magnetic field, I the intensity of magnetization, treated as magnetic moment per unit volume, T the absolute temperature, and R' a constant which is the reciprocal of Curie's constant (the product of the magnetic susceptibility and the absolute temperature). This equation as written above implies that the intensity of magnetization may increase indefinitely with the magnetizing field, which conflicts with the fact that the intensity has a limit. The equation must therefore be extended to include this fact and we write it as follows:—

$$H\left(\frac{1}{I} - \frac{1}{I_0}\right) = R'T, \quad (2)$$

where I_0 is the limiting or maximum intensity of magnetization.

In order to pass from paramagnetism to ferromagnetism two other facts must be recognized: first, that the intensity of magnetization becomes 10^6 to 10^7 times larger than in the paramagnetic state and secondly, that hysteresis is in general in evidence. Both these facts may be incorporated

* Communicated by the Author.

in the equation if a term $a'I^2$ be added to H , which is equivalent to the addition of an intrinsic field, and we write,

$$(H + a'I^2) \left(\frac{1}{I} - \frac{1}{I_0} \right) = R'T, \quad . \quad . \quad . \quad (3)$$

which is an equation applying to ferromagnetic susceptibility. By multiplying all through by I_0^2 and writing R for $R'I_0^2$ *, we obtain the energy equation to ferromagnetism, which may conveniently be put,

$$(HI_0 + a'I_0I^2) \left(\frac{I_0}{I} - 1 \right) = RT. \quad . \quad . \quad . \quad (4)$$

The first bracket represents energy in terms of magnetic quantities, the second bracket represents the fractional part of that energy, and the quantity RT has the same significance as in the gas equation and expresses thermal energy.

Reverting to equation (3), it has been shown† that it is only an extremely small part of the intrinsic field which is a genuine magnetic field, and that the larger part, which is indeed approximately the whole, is of another kind and makes its appearance in virtue of energy considerations. The intrinsic field is therefore of a dual nature and a' , the constant of this field, must be separated into two parts, a_1 for the magnetic part and c for the other part, so that $a' = a_1 + c$; but inasmuch as a_1 is negligible compared with c we shall not make an appreciable error in putting a' for c .

We now write equation (3) in two parts as follows:—

$$(H + a_1I^2) \left(\frac{1}{I} - \frac{1}{I_0} \right) = R_1T \quad . \quad . \quad . \quad (5)$$

$$\text{and} \quad a'I^2 \left(\frac{1}{I} - \frac{1}{I_0} \right) = R'T. \quad . \quad . \quad . \quad (6)$$

Here in equation (5) we have replaced R' in equation (3) by R_1 in order to give suitable values when the non-magnetic field is omitted, and the equation then involves only magnetic quantities and is applicable to ferromagnetism when H and I are the variables. In equation (6) we have written a' for c and have omitted H , which is in general negligible compared with $a'I^2$ (except at temperatures above the critical temperature when I becomes very small), and the equation then applies to $I = f(T)$.

* For nickel $R/2$ must be written for R —see *Phil. Mag.* vol. xxxvi. p. 351.

† *Phil. Mag.* vol. xliii. p. 401.

If, in equation (5), we suppress magnetic hysteresis in any of the recognized ways, then the term $a_1 I^2$ disappears, and the equation for anhysteretic isothermals is

$$H \left(\frac{1}{I} - \frac{1}{I_0} \right) = R_1 T. \quad . \quad . \quad . \quad . \quad (7)$$

It is analogous to the complete equation to paramagnetism (equation (2)) and only differs from it in that R_1 replaces R' .

It becomes a matter of theoretical interest to find values for the coefficients a_1 and R_1 in the ferromagnetic equation (5) and to compare them with a' and R' .

2. We have seen that the suppression of hysteresis eliminates the unknown quantity a_1 and equation (7), which then results, involves only the unknown quantity R_1 . We begin, therefore, by tracing anhysteretic curves at constant temperatures for the determination of R_1 .

In a former investigation* such curves were traced for iron and nickel at different temperatures and the suppression of hysteresis was effected by running an alternating current through the magnetic material all the time it was under examination; this method was suitable for bringing out certain general features which were then being investigated, but it yields values for the intensity of magnetization which are lower than the truth and the results so obtained cannot be used here.

An easy and effective method of suppressing hysteresis is to heat the ferromagnetic material, at any given field strength, above its critical temperature and allow it to cool to the required temperature. This procedure was now adopted with this modification: instead of heating and cooling at each step of the magnetizing process, a set of curves at a number of different field strengths was plotted as the specimen cooled after being raised above its critical temperature, and from these curves another set was constructed, each curve giving the anhysteretic values of I for different field strengths at some one temperature.

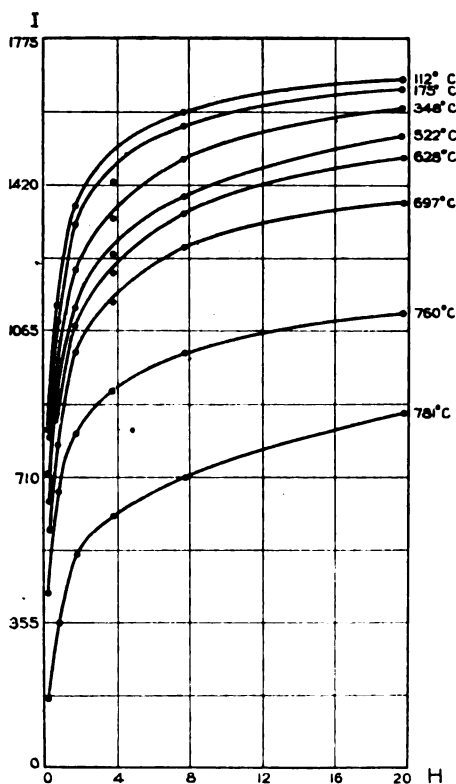
The experiments were made on well annealed wires of iron and nickel, the iron wire being 18.9 cm. in length and 0.056 cm. in diameter, and the nickel wire 19.0 cm. in length and 0.088 cm. in diameter; they were inserted singly in a long solenoid and the intensity of magnetization was determined by a sensitive astatic mirror magnetometer. In

* Ashworth, Phil. Mag. xxvii. p. 357 (Feb. 1914).

general the arrangements for heating and the other details of the experiment were the same as those described in the paper on the "Anhyseretic properties of Iron and Nickel," to which reference has been made*.

3. Diagram I. exhibits anhyseretic curves of iron

Diagram I.—Anhyseretic isothermals of Iron.



determined in this way from cooling curves. Applying the equation

$$H \left(\frac{1}{I} - \frac{1}{I_0} \right) = R_1 T$$

to these anhyseretic curves we find for the most probable

* Phil. Mag. xxvii. p. 357 (Feb. 1914).

values of R_1 , at the temperatures given below, the following numbers :—

C°.	A°.	$R_1 \times 10^6$.
112	385	0.67
175	448	0.64
348	621	0.57
370	643	0.57
522	795	0.54
628	901	0.53
760	1033	0.62

$$\text{Mean} = 0.59 \times 10^{-6}$$

Each of the values of R_1 has been arrived at by selecting five or six points on the curve and treating the equations formed from them by the method of least squares. Corrections for self-demagnetization have been made. The mean value 0.6×10^{-6} for R_1 receives confirmation from an experiment by Ewing* on the magnetization of very soft annealed iron wire under vibration by tapping. He remarks that under these circumstances an initial permeability of about 80,000 is found and, treating the air temperature at which the experiment was made as 15° C., this gives a value for R_1 of 0.55×10^{-6} .

The paramagnetic constant R' , which is the reciprocal of Curie's constant, is 3.56 when the intensity of magnetization is treated as magnetic moment per unit volume, and we have therefore for the ratio of R' to R_1 ,

$$\frac{R'}{R_1} = \frac{3.56}{0.6} \times 10^6 = 5.9 \times 10^6.$$

The kinetic energy of two degrees of freedom per unit of temperature per cubic centimetre of iron is

$$R = \frac{83.2 \times 10^6}{55.85} \times 7.86 = 11.7 \times 10^6,$$

the atomic weight of iron being 55.85 and the density 7.86, and the number just found for the ratio of R' to R_1 is almost exactly the half of this, so that numerically we have

$$\frac{R'}{R_1} = \frac{R}{2} \dots \dots \dots (8)$$

* Ewing, 'Magnetic Induction in Iron and other Metals,' p. 115, 1894.

4. Having obtained a value for R_1 , we can now make a determination of a_1 . If in the ferromagnetic hysteric equation

$$(H + a_1 I^2) \left(\frac{1}{I} - \frac{1}{I_0} \right) = R_1 T,$$

we put H equal to zero, then I is the residual intensity of magnetization (I_r) and we get

$$a_1 I_r^2 \left(\frac{1}{I_r} - \frac{1}{I_0} \right) = R_1 T. \quad . \quad . \quad . \quad (9)$$

But we may also write, when the residual magnetism is regarded as a function of the temperature,

$$a' I_r^2 \left(\frac{1}{I_r} - \frac{1}{I_0} \right) = R' T;$$

and it follows that

$$\frac{a'}{a_1} = \frac{R'}{R_1}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and therefore

$$a_1 = a' \frac{R_1}{R'}.$$

The values on the right-hand side of this equation are :

$$a' = 7.00, \quad R' = 3.56, \quad R_1 = 0.6 \times 10^{-6},$$

and consequently

$$a_1 = 1.2 \times 10^{-6}.$$

It follows from equation (10) that

$$\frac{a'}{a_1} = \frac{R}{2},$$

since

$$\frac{R'}{R_1} = \frac{R}{2}.$$

There is another method which allows a_1 to be estimated, and may be used to corroborate the result just obtained. The anhyseretic equation, when the intensity of magnetization has the residual value I_r , is

$$H \left(\frac{1}{I_r} - \frac{1}{I_0} \right) = R_1 T,$$

and the hysteretic equation is

$$a_1 I_r^2 \left(\frac{1}{I_r} - \frac{1}{I_0} \right) = R_1 T$$

when H is zero. By division we get

$$H = a_1 I_r^2,$$

and therefore

$$a_1 = \frac{H}{I_r^2}.$$

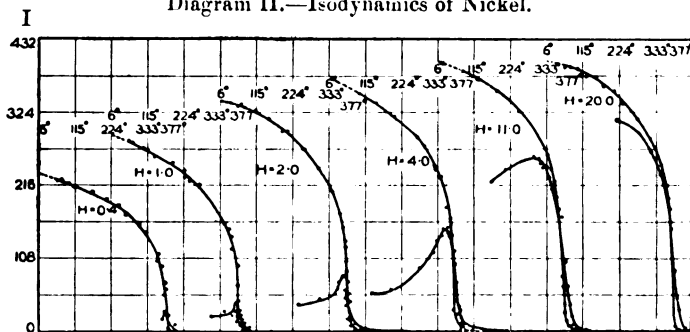
Observations give $H=2.0$ on the anhysteretic curve when $I_r=1350$. Hence

$$a_1 = \frac{2.0}{1350^2} = 1.1 \times 10^{-6}.$$

This method of determining a_1 involves the square of the residual intensity, and the probable error in the evaluation of a_1 is larger than in the first method. The former result, 1.2×10^{-6} , is for this reason to be preferred.

5. Experiments made on nickel in the same way as on iron yield results of a like kind. Anhysteretic curves of

Diagram II.—Isodynamics of Nickel.



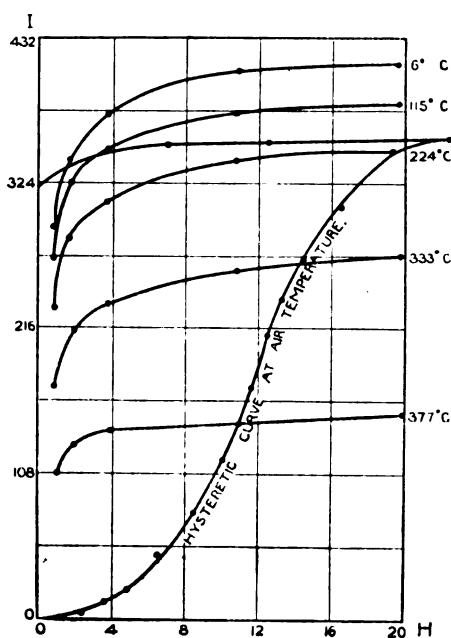
nickel, derived from the isodynamic curves of Diagram II., corrected for self-demagnetization, are shown in Diagram III., and from these and others, not shown in the diagram, the

following values of R_1 at the subjoined temperatures are derived :—

C°.	A°.	$R_1 \times 10^6$.
6	279	3.11
107	380	3.09
115	388	2.69
200	473	2.35
224	497	2.35
292	565	3.78
333	606	3.61
377	650	4.23

Mean 3.15×10^{-6}

Diagram III.—Anhyseretic isothermals of Nickel.



R' for nickel, calculated from Curie's constant, is 20.8 and the ratio of R' to R_1 is

$$\frac{R'}{R_1} = \frac{20.8}{3.2} \times 10^6 = 6.5 \times 10^6.$$

The constant R for nickel, obtained in the same way as for iron, is 12.6×10^6 , and the half of this, namely 6.3×10^6 , is nearly the ratio of $\frac{R'}{R_1}$, and so again we have

$$\frac{R'}{R_1} = \frac{R}{2} \dots \dots \dots (11)$$

6. The determination of a_1 may be made from the equation

$$\frac{a'}{a_1} = \frac{R'}{R_1}$$

Putting $R_1 = 3.2 \times 10^{-6}$ as above, $a' = 83.7$ and $R' = 20.8$, we get

$$a_1 = 13.3 \times 10^{-6}.$$

For the corroboration of this value, we may use the alternative method which was employed in this connexion with iron. We then have

$$a_1 = \frac{H}{I_r^2},$$

where H is the anhysteretic value of the field for intensity equal to I_r .

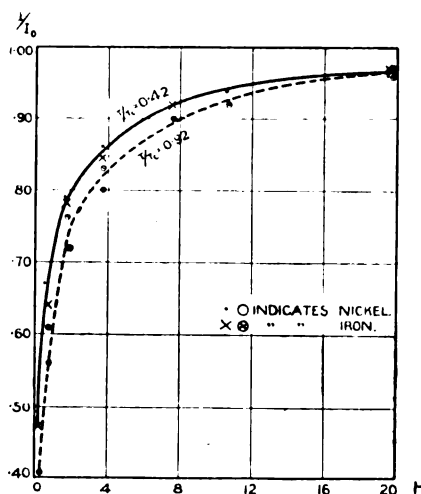
In Diagram III. a hysteretic curve has been traced in addition to the anhysteretic curves, and from this I_r is found to be 320 and the corresponding anhysteretic field is 1.3 units. Hence

$$a_1 = 12.7 \times 10^{-6}.$$

6. The equations of both iron and nickel have the same general form and they differ only in having different constants. By constructing a reduced equation for each of these metals the theory of corresponding states should then apply. In Diagram IV. anhysteretic reduced values of the intensity of magnetization, calculated as a fraction of the value at absolute zero and at a field-strength of 20 units, have been marked on the vertical axis, and *observed* field-strengths on the horizontal axis. It is sufficient to mark observed field strengths because calculation shows that the critical field is the same in magnitude for iron and nickel and their reduced field strengths must therefore be the same for any observed field strength. It is, however, necessary to use reduced temperatures as the critical temperatures of iron and nickel are not the same, and this has been done.

Points from an anhyseretic curve of iron at 175° C. have been plotted along with points from an anhyseretic curve of nickel at 6° C., these temperatures being corresponding temperatures and having a reduced value of 0.42; and it will be seen that a single curve runs evenly through all of them. Similarly another single curve at the reduced temperature of 0.92, which corresponds to 697° C. for iron and 333° C. for nickel, runs evenly through reduced anhyseretic values of intensity of magnetization. Thus the principle of corresponding states applies to anhyseretic curves of $I = \phi(H)$ for iron and nickel.

Diagram IV.—Curves $I/I_0 = \phi(H)$ at reduced temperatures for Iron and Nickel.



7. It has been shown in a former paper * that the maximum intensity of magnetization (I_0) can be successfully calculated from the equation

$$R = R' I_0^2 \quad (12)$$

when iron is the ferromagnetic material. Also, we have found above by equation (8) that

$$R = 2 \frac{R'}{R_1}$$

* "On the Calculation of Magnetic and Electric Saturation Values," Phil. Mag. xxxvi. p. 351 (October 1918).

and it at once follows that

$$\frac{2}{R_1} = I_0^2.$$

Numerically, we have

$$\frac{2}{R_1} = \frac{2}{0.6} \times 10^6 = 3.3 \times 10^6,$$

$$I_0^2 = 1817^2 = 3.3 \times 10^6.$$

Thus with iron,

$$R_1 I_0^2 = 2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

When nickel is the ferromagnetic material equation (12) must be written

$$\frac{R}{2} = R' I_0^2,$$

and this combined with (11) leads to

$$\frac{1}{R_1} = I_0^2.$$

The numerical verification is

$$\frac{1}{R_1} = \frac{1}{3.2} \times 10^6 = 0.31 \times 10^6,$$

$$I_0^2 = 552^2 = 0.305 \times 10^6.$$

Thus with nickel,

$$R_1 I_0^2 = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

8. The expression $R_1 I_0^2$ relates to the energy per unit of temperature in the ferromagnetic state below the critical temperature, while $R' I_0^2$ is the energy per unit of temperature above the critical temperature. Now R_1 is negligible compared with R' and therefore it follows that the change of energy per unit of temperature on passing through the critical temperature is $R' I_0^2$. This is equal to R for iron and $R/2$ for nickel and hence we may say:—

When iron or nickel passes through the critical temperature there is a change of kinetic energy per unit of temperature equivalent to that of *two degrees of freedom*, the molecular weight of iron being 55.85 and that of nickel 2×58.68 above the critical temperature.

This change of energy is found to be simply and intimately connected with the discontinuity of the true specific heat at the critical temperature.

9. A table of the symbols used in this paper and their numerical values together with some of the more important relations subsisting between them is subjoined.

		IRON.	NICKEL.
Critical Temperature	T_c	1058°A	661°A
Maximum Intensity of Magnetization ...	I_0	1817	552
Paramagnetic Constant	R'	3.56	20.8
Intrinsic Field Constant	a'	7.0	83.7
Ferromagnetic Constant	R_1	0.6×10^{-6}	3.2×10^{-6}
Ferromagnetic Field Constant	a_1	1.2×10^{-6}	13.3×10^{-6}
Gas Constant.....	R	11.7×10^8	12.6×10^8
True Specific Heat at the Critical Temperature	c_θ	0.309	0.154

EQUATIONS :--

	IRON.	NICKEL.
$T_c = \frac{8}{27} \frac{a' I_0}{R'}$	$R' I_0^2 = R.$	$R' I_0^2 = \frac{R}{2}.$
$R_1 = \frac{R'}{R/2}$	$R_1 I_0^2 = 2.$	$R_1 I_0^2 = 1.$
$a_1 = a' \frac{R_1}{R} = \frac{a'}{R/2}$		

LXXXIII. *An Automatic Feeder for Coloured Flames.* By J. J. MANLEY, M.A., *Research Fellow, Magdalen College, Oxford* *.

IN a former paper † a simple device was described for maintaining the coloured flames required for polarimetric and spectroscopic work. Recent experiments with replicas of the original apparatus have shown that in general it is difficult to establish the conditions required for a slow and uniform flow of salt solution through the platinum wire wick. When the flow is not suitably restricted, considerable spurting occurs: this is not only highly inconvenient, but also harmful to adjacent instruments. These defects are

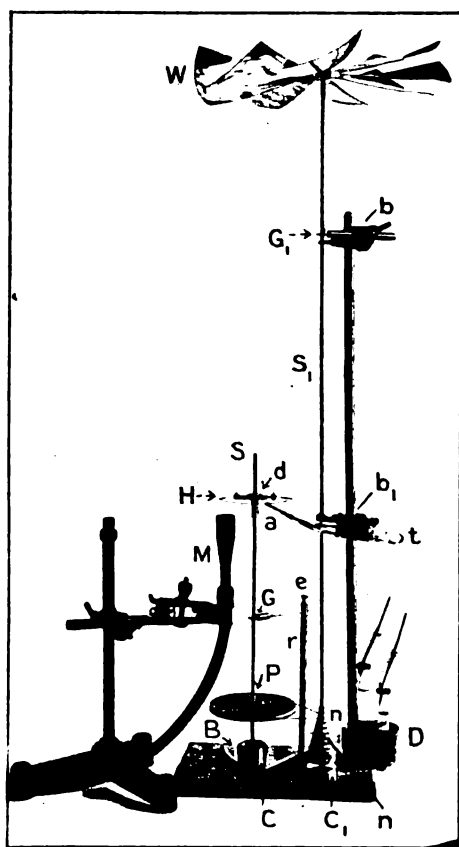
* Communicated by the Author.

† Phil. Mag. xlv. p. 336 (Feb. 1923).

not experienced with the new and more elaborate automatic feeder illustrated in fig. 1.

The base of the feeder is an ordinary iron retort-stand having a rectangular foot 20 cm. long and 13 cm. wide and a rod 60 cm. high. Two bosses, b , b_1 , are clamped to

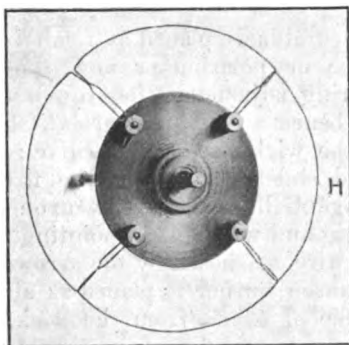
Fig. 1.



the rod; the one, b , carries a brass guide G_1 for the steel rod S_1 , and the other, b_1 , a tubular holder for the glass reservoir t , containing the salt solution for colouring the flame. The upper end of S_1 is fitted with eight inclined and curved sectors of aluminium: the lower end is glass-hard and sharply pointed, and it rests within a conical oil-charged hole in a brass block C_1 screwed to the base. This part of the apparatus is therefore very similar to that used for

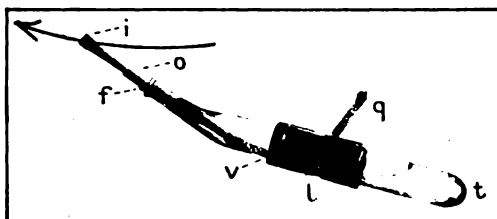
actuating the stirrer in an Ostwald thermostat. *S* is another steel rod similar to but shorter than *S*₁: its hardened point also rests within a brass oil-containing cup *C* soldered to the plate *B*. The rod is supported by the guide *G*, which, after adjustment, is fastened by the screw *e*. Attached to *S*

Fig. 2.



are (1) a light pulley *P*₁, cord driven by any one of the several pulleys formed upon the boxwood cone *n*, and (2) a brass disk *d* fitted with screw bolts and nuts; these hold the ends of the four radiating arms of a platinum wire ring *H* (fig. 2). The supporting rod *r* passes first through the brass plate *B* to which it is soldered, and then through the hole in the iron base: in this position it is stiffly held by a washer and nut. Thus the plate *B*, with *r* as a pivot, can be turned to the right or left, and the tension of the driving-cord thereby diminished or increased. A large burner of

Fig. 3.



the Meker or Fisher type is placed with its top 1 or 2 cm. below the platinum-wire ring. The glass reservoir *t* and its holder *l* are, for the sake of clearness, shown detached in fig. 3. The neck of the reservoir contains a loosely-fitting glass wick holder *o* having a small bulb *f* resting within

the lipped opening. The wick *i* is of silky and compact asbestos fibre, rendered pliable by drawing it between the thumb and fore finger; it is broadened out at *i* to ensure continuous contact with the platinum-wire ring. The rubber band *v* prevents the reservoir from slipping in its holder; the arm *q* is held by the boss *b* (fig. 1). The feeder is adjusted and brought into use in the following way:—

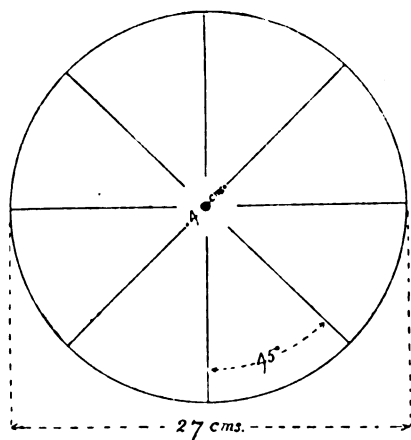
First, the apparatus is placed at a suitable distance from the spectroscope or polarimeter and the height of the platinum-wire ring adjusted; the ring is then secured to *S* by a screw beneath the disk. Next, the reservoir *t* is inclined until the wick becomes effective; it is then raised or lowered, and slued round until the flat portion of the wick bears tangentially and lightly upon the outside of the platinum ring and with its top pointing in the direction of the receding wire, as shown by the arrowed line in fig. 3. Finally, the Bunsen burner is placed as already described, and at a distance of 4 cm. from the wick. On kindling the gas, the hot air ascending from the flame actuates the vane system above, with the result that the platinum ring is continuously rubbed by the salt-charged wick and passed through the flame, thus producing a non-intermittent and intense coloration. As the successive portions of the ring are still hot when they again reach the wick, a more or less dry residue is carried into the flame: in this way any spurting is altogether negligible. When not in use, the reservoir is placed in an upright position by suitably rotating the arm *q* (fig. 3). The wire ring is cleaned by continuing the application of the flame after the removal of the wick. For convenience, several reservoirs each containing a different salt solution may be prepared. Idle reservoirs are placed in the circular apertures of the block *D* (fig. 1), through which the iron rod of the stand passes and to which it affords support.

For those desiring to construct automatic feeders for their own use, the following additional details may be helpful. And here we remark that the best results are obtained only when the several moving parts of the apparatus are given certain relative dimensions. If, for example, the vane system *W* is too small, the speed is excessive; also the driving-power is insufficient to overcome the friction between the wire and the wick. The dimensions named below have proved entirely satisfactory.

1. *The Vanes*.—The driving system is made from an aluminium disk 27 cm. in diameter and 0.5 mm. thick.

The disk is cut into eight equal sectors, as shown in fig. 4; the cuts terminate at points 2 cm. from the centre. The sectors are turned so as to form an angle of about 45° with the original plane surface and then gently curved, as seen in fig. 1. Made thus, the system possesses considerable strength, and is not readily distorted or damaged. In these

Fig. 4.



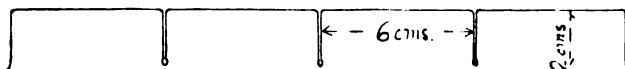
respects it is superior to the usual Ostwald pattern, which is built up from individual sections of much thinner sheet; moreover, rivetting is entirely avoided.

2. *The Rods S, S₁.*—These are of tool steel 4 mm. in diameter. Suitable lengths are 35 cm. for S and 75 for S₁: the former enables one to adjust the height of the platinum ring for almost any spectroscope or polarimeter without the aid of blocks. The length of S₁ places the vanes well above, and out of the way of other apparatus.

3. *The Disk d.*—This is 46 mm. in diameter and 1 mm. thick. It is drilled at four equidistant points near the edge for the reception of small screw bolts and nuts, as shown in fig 2. (No. 8 B.A. bolts are convenient.)

4. *The Platinum-wire Ring.*—The ring is formed from one

Fig. 5.



piece of wire 40 cm. long and 0.5 mm. in diameter. First, the wire is bent as indicated in fig. 5, and then made

approximately circular, with the four twinned arms directed towards the centre. Next, the inner extremities of the arms are secured by their respective nuts, and the wire ring is made truly circular. Prepared thus, the ring has a diameter of about 8 cm. Additional rigidity is imparted by bending and crossing the twinned arms, as seen in fig. 2. If the arms are bent gently downwards they are not traversed by the solution from the wick.

5. *The Pulleys*.—The pulley P is 9 cm. in diameter and 7 mm. or less thick; it is of mahogany and well covered with shellac varnish. The boxwood cone *n* tapers from a diameter of 26 mm. to one of 8 mm. Eight grooves are cut in it, and these range in diameter from 22 to 5 mm. The groove 8 mm. in diameter gives excellent results; with it the wire makes three revolutions per minute: its velocity is therefore 12 mm. per second.

6. *The Driving-cord*.—The driving-cord should be chosen with care. After trying various cords, a single thread of Manilla hemp composed of some four to six fibres was found superior to all others. The thread is glossy and tough and not easily frayed; and as its diameter is about 0.3 mm. only, the knot formed by tying the ends is too small to disturb the smooth running of the apparatus.

6. *The Reservoirs*.—These are conveniently made from glass tubing 12 mm. in diameter. The body may be 8 cm. and the neck 3 cm. long.

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LXXXIV. *On Mr. T. Smith's Formulæ for Oblique Focal Distance in Terms of Magnification.* By ALICE EVERETT, M.A. (From the National Physical Laboratory.) *

NEAR the end of a paper on Ray Tracing (Proc. Phys. Soc. vol. xxx. p. 232, 1918) Mr. T. Smith gives, merely incidentally and without proof, new formulæ for finding the position of either member of a pair of conjugate primary foci in terms of the magnification, on a ray traced through a coaxial lens system. The present writer has had occasion to employ these formulæ, and, since results based on statements of which no proof has been published may be regarded as incomplete, ventures here to offer a proof of her

* Communicated by the Author.

own, together with some remarks on the corresponding formulæ for secondary foci by the same author (*Ibid.* vol. xxvii. p. 508, 1915).

Preliminary Note on some Properties of certain Sequence Formulæ employed in the Proof.

Suppose p'_λ, q'_λ and p''_λ, q''_λ to be representative terms of two different series of quantities both satisfying the following relations

$$p_\lambda = a_\lambda p_{\lambda-1} - b_{\lambda-1} q_{\lambda-1}, \quad q_\lambda = c_\lambda q_{\lambda-1} + d_{\lambda-1} p_{\lambda-1} \quad (1)$$

then it is known that

$$\frac{p'_\lambda q''_{\lambda-1} - p''_\lambda q'_\lambda}{p'_{\lambda-1} q''_{\lambda-2} - p''_{\lambda-1} q'_{\lambda-2}} = a_\lambda c_\lambda, \quad (2)$$

regardless of the values of the b 's and d 's. This can easily be proved by actual substitution.

Hence

$$\frac{(p'_\lambda q'' - p'' q')_\lambda}{(p'_\lambda q'' - p'' q')_1} = \prod_{\lambda=2}^{L_t=n} a_\lambda c_\lambda, \quad (3)$$

Π signifying continued product.

Corollary.—If $a_\lambda = c_\lambda = 1$ for all values of λ , then

$$(p'_\lambda q'' - p'' q')_\lambda = \text{constant} = p'_1 q''_1 - p''_1 q'_1 \quad (3A)$$

It is evident that p_λ, q_λ can be written in the forms

$$p_\lambda = \alpha_\lambda p_0 + \beta_\lambda q_0, \quad q_\lambda = \gamma_\lambda p_0 + \delta_\lambda q_0.$$

Hence, when $q_0 = 0$, we have $p_\lambda = p_0 \alpha_\lambda, \quad q_\lambda = p_0 \gamma_\lambda$;

and when $p_0 = 0$, we have $p_\lambda = q_0 \beta_\lambda, \quad q_\lambda = q_0 \delta_\lambda$.

Clearly α_λ and γ_λ are the values of p_λ and q_λ when $p_0 = 1$ and $q_0 = 0$; and $\beta_\lambda, \delta_\lambda$ are the values of p_λ, q_λ when $p_0 = 0, q_0 = 1$.

Hence, when $q_0 = 0$,

$$\left. \begin{aligned} p_\lambda &= p_0 (\text{value of } p_\lambda \text{ for } p_0 = 1), \\ q_\lambda &= p_0 (\quad , \quad , \quad q_\lambda \quad , \quad , \quad); \\ \text{and when } p_0 &= 0, \\ p_\lambda &= q_0 (\text{value of } p_\lambda \text{ for } q_0 = 1), \\ q_\lambda &= q_0 (\quad , \quad , \quad q_\lambda \quad , \quad , \quad). \end{aligned} \right\} \quad (4)$$

Nomenclature.

The quasi-differential notation of the original has been renounced for reasons of economy, and some other slight alterations of nomenclature have been found expedient.

The letters employed have the following significations :—

ϕ_λ , ϕ'_λ are the angles of incidence and refraction at the λ th surface.

ψ_λ is the inclination of the ray to the optic axis after λ refractions.

μ_λ is the refractive index of the λ th medium.

t_λ is the length of path in the λ th medium.

$k_\lambda = k'_\lambda \cos \phi_\lambda \cos \phi'_\lambda = (\mu_\lambda \cos \phi'_\lambda - \mu_{\lambda-1} \cos \phi_\lambda) / r_\lambda$.

p_λ , q_λ for the axial section are the distances of object and image points from the λ th surface, measured along the ray in the direction light travels. (The object point here is the image formed by the previous $\lambda - 1$ surfaces. p and q here have nothing to do with the p and q in the preliminary note, and will not be used in a way likely to cause confusion.)

P is the value of p_1 for $q_n = \infty$.

Q is the value of q_n for $p_1 = -\infty$.

η_λ , η'_λ are the perpendiculars from the λ th point of incidence upon the consecutive ray in the axial section before and after incidence.

m is the magnification perpendicular to the ray of a linear element in the axial section.

P and Q may be otherwise defined as the distances of the principal oblique foci along the ray from the first and last surfaces of the lens.

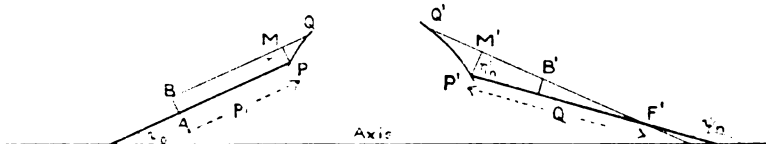
In discussing the sagittal section, and secondary foci, p , q , P , Q are replaced by u , v , U , W , and m by ν .

I. Formulæ for the Primary Focal Distances.

The discussion of the primary foci is confined to rays in an axial plane.

In the figure, $AP \dots P'A'F'$ is the chief ray, F' the second principal oblique focus. BMQ is a very near ray parallel to AP ; therefore its path $Q'B'$ after refraction passes through F' . P , Q are the points of incidence of the two rays, and P' , Q' their points of emergence. $PM = \eta_1$ and $P'M' = \eta'_n$ are drawn perpendicular from P , P' to the near ray. $AB = \eta_1$ is a line

element perpendicular to the incident ray; $A'B'$ is drawn from A' , the image of A , perpendicular to the refracted chief ray.



Then m , the magnification in the axial plane, is defined as the ratio of $A'B'$ to AB .

Let $P'F' = Q$, $AP = p_1$, $P'A' = q_n$.
Then

$$AB = PM = \eta_1, \quad A'B' = P'M' \frac{A'F'}{P'F'} = \eta'_n \frac{(Q - q_n)}{Q};$$

$$\therefore m = \frac{A'B'}{AB} = \frac{\eta'_n (Q - q_n)}{\eta_1 Q}. \quad \text{Also } Q d\psi_n = -\eta'_n;$$

$$\therefore q_n = Q - m \frac{Q\eta_1}{\eta'_n} = \frac{-\eta'_n}{d\psi_n} + m \frac{\eta_1}{d\psi_n}.$$

If $\eta_\lambda, \eta'_\lambda$ be the perpendiculars from the point of intersection of the chief ray with the λ th surface upon the consecutive ray before and after incidence, and ds the element of arc PQ , then $\eta'/\cos \phi' = \eta/\cos \phi = ds$ for any value of λ .

Hence, substituting for η'_n , we have

$$\frac{q_n}{\mu_n} = - \left(\frac{\eta}{\mu n d\psi} \cdot \frac{\cos \phi'}{\cos \phi} \right)_n + \frac{m\eta_1}{\mu_n d\psi_n} \dots \dots (5)$$

Similarly, if instead of taking $d\psi = 0$ (*i. e.* the incident rays parallel), we take $d\psi_n = 0$ (*i. e.* the emergent rays parallel), we obtain

$$\frac{p_1}{\mu_0} = - \left(\frac{\eta'_1}{\mu_0 d\psi_0} \cdot \frac{\cos \phi_1}{\cos \phi'_1} \right) + \frac{\eta'_n}{m\mu_0 d\psi_0} \dots \dots (6)$$

Now $\eta_\lambda - \eta'_{\lambda-1} = t_{\lambda-1} d\psi_{\lambda-1};$

$$\therefore \eta_\lambda - \eta_{\lambda-1} \frac{\cos \phi'_{\lambda-1}}{\cos \phi_{\lambda-1}} = t_{\lambda-1} d\psi_{\lambda-1} \dots \dots (7)$$

and

$$\eta'_{\lambda-1} - \eta'_\lambda \frac{\cos \phi_\lambda}{\cos \phi'_\lambda} = -t_{\lambda-1} d\psi_{\lambda-1} \dots \dots (8)$$

Also $k_\lambda \cdot ds_\lambda = k'_\lambda \eta_\lambda \cos \phi'_\lambda = k'_\lambda \eta'_\lambda \cos \phi_\lambda$

$$\begin{aligned}
 &= (\mu_\lambda \cos \phi'_\lambda - \mu_{\lambda-1} \cos \phi_\lambda) d(\phi' - \psi)_\lambda \\
 &= \mu_\lambda \cos \phi'_\lambda (d\phi'_\lambda - d\psi_\lambda) - \mu_{\lambda-1} \cos \phi_\lambda (d\phi_\lambda - d\psi_{\lambda-1}),
 \end{aligned}$$

since $\phi'_\lambda - \phi_\lambda = \psi_\lambda - \psi_{\lambda-1}$,

$$= -\mu_\lambda \cos \phi'_\lambda d\psi_\lambda + \mu_{\lambda-1} \cos \phi_\lambda d\psi_{\lambda-1},$$

because

$$\begin{aligned}
 \mu_\lambda \cos \phi'_\lambda d\phi'_\lambda - \mu_{\lambda-1} \cos \phi_\lambda d\phi_\lambda \\
 = d(\mu_\lambda \sin \phi'_\lambda - \mu_{\lambda-1} \sin \phi_\lambda) = 0;
 \end{aligned}$$

$$i. e., \quad \mu_\lambda d\psi_\lambda - \mu_{\lambda-1} d\psi_{\lambda-1} \frac{\cos \phi_\lambda}{\cos \phi'_\lambda} = -k'_\lambda \eta_\lambda, \quad \dots \quad (9)$$

$$\mu_{\lambda-1} d\psi_{\lambda-1} - \mu_\lambda d\psi_\lambda \frac{\cos \phi'_\lambda}{\cos \phi_\lambda} = k'_\lambda \eta'_\lambda. \quad \dots \quad (10)$$

(7) and (9) may be used to find η_n and $\mu_n d\psi_n$ in (5); and (8) and (10) to find η'_1 and $\mu_0 d\psi_0$ in (6), calculating in the reverse direction.

Either pair of equations (7, 9) or (8, 10) is of the type (1) mentioned in the preliminary note, $-\eta$ corresponding to p , and $\mu d\psi$ to q . Hence by (4), if $d\psi_0 = 0$, and G_λ, H_λ denote the special values of $-\eta_\lambda, \mu_\lambda d\psi_\lambda$ given by (7) and (9) for the initial value $-\eta_0 = 1$, then the values of $-\eta_\lambda, \mu_\lambda d\psi_\lambda$ for any initial value of η are

$$-\eta_\lambda = -\eta_0 G_\lambda \quad \text{and} \quad \mu_\lambda d\psi_\lambda = -\eta_0 H_\lambda.$$

We assume $\eta_1 = \eta_0$, since the initial rays are parallel, and any imaginary surface crossed by the ray before it reaches the first surface would cause no refraction. Thus

$$-\eta_\lambda = -\eta_1 G_\lambda \quad \text{and} \quad \mu_\lambda d\psi_\lambda = -\eta_1 H_\lambda.$$

Incidentally it may be mentioned that, corresponding to the values $-\eta_0 = 1, \mu_0 d\psi_0 = 0$, equations (7) and (9) give $-\eta_1 = 1, \mu_1 d\psi_1 = k'_1$.

From the values just found for $-\eta_\lambda, \mu_\lambda d\psi_\lambda$, it follows that

$$\frac{-\eta_n}{\mu_n d\psi_n} = \frac{G_n}{H_n}, \quad \frac{-\eta_1}{\mu_n d\psi_n} = \frac{1}{H_n}.$$

Inserting these values in (5), it becomes

$$q_n = \frac{G_n \cos \phi'_n}{H_n \cos \phi_n} - \frac{m}{H_n} \quad \dots \quad (11)$$

Treating (6) on similar lines, but reckoning backwards and starting with $-\eta'_n, \mu_n d\psi_n = 0$ as initial quantities, it becomes

$$\rho_1 = -\frac{G_1' \cos \phi_1}{H_n \cos \phi_1'} + \frac{1}{m H_n}, \quad (12)$$

where G_1', H_n are the values of $-\eta_1', \mu_0 d\psi_0$ that would be obtained if $-\eta'_n = 1, \mu_n d\psi_n = 0$. G_n, G_1', H_n are ray constants. (11) and (12) are Mr. T. Smith's formulæ.

It may perhaps be instructive to compare the foregoing with the following analysis.

From the well-known formula for refraction at a single (the λ th) surface,

$$\frac{\mu_\lambda \cos^2 \phi'_n}{q_\lambda} - \frac{\mu_{\lambda-1} \cos^2 \phi_\lambda}{p_\lambda} = k_\lambda,$$

where $p_\lambda = q_{\lambda-1} - t_{\lambda-1}$, it is evident (and may be proved by induction) that q_λ is of the form

$$\frac{A_\lambda + C_\lambda p_1}{B_\lambda + D_\lambda p_1}.$$

This expression, however, does not give neat results, and we therefore take new variables:

$$p'_\lambda = \frac{1}{\mu_{\lambda-1}} \left(\frac{p}{\epsilon \cos^2 \phi'_\lambda} \right), \quad q'_\lambda = \left(\frac{q}{\mu \epsilon \cos^2 \phi'} \right)_\lambda,$$

leaving the significance of the constant ϵ for future consideration, and write

$$q'_\lambda = \frac{E_\lambda + G_\lambda p'_1}{F_\lambda + H_\lambda p'_1} \quad (13)$$

Substituting the corresponding expression for $q'_{\lambda-1}$ in the equation of refraction, and comparing coefficients in the two expressions for q'_λ , we find the following relations between the G 's and H 's,

$$\left. \begin{aligned} f'_\lambda G_\lambda &= G_{\lambda-1} \epsilon_{\lambda-1} \cos^2 \phi'_{\lambda-1} - \left(H_{\mu}^t \right)_{\lambda-1}, \\ f'_\lambda H_\lambda &= H_{\lambda-1} \epsilon_\lambda \cos^2 \phi_\lambda + (k \epsilon G)_\lambda, \end{aligned} \right\} \quad (14)$$

where f'_λ is another undetermined constant. Similar relations connect the E 's and F 's.

(13) is equivalent to

$$\left(q'_\lambda - \frac{G_\lambda}{H_\lambda}\right)\left(p'_1 + \frac{F_\lambda}{H_\lambda}\right) = \left(\frac{EH - FG}{H^2}\right)_\lambda. \quad (15)$$

It is desirable to select the constants ϵ and f so as to give a convenient expression for $EH - FG$ in (15), besides rendering the equations (14) as simple as possible.

By (3)

$$\frac{(EH - FG)_\lambda}{(EH - FG)_1} = \frac{\left(\prod_{\lambda=1}^{L=t} \frac{\epsilon_\lambda}{f_\lambda} \cos \phi_\lambda \cos \phi'_\lambda\right)^2}{\epsilon_1 \epsilon_\lambda \cos^2 \phi_1 \cos^2 \phi'_\lambda}.$$

A glance shows that matters will be simplified by putting

$$f_\lambda = 1, \quad \frac{1}{\epsilon_\lambda} = \cos \phi_\lambda \cos \phi'_\lambda.$$

Equations (14) then become

$$\left. \begin{aligned} G_\lambda &= G_{\lambda-1} \frac{\cos \phi'_{\lambda-1}}{\cos \phi_{\lambda-1}} - \left(H \frac{t}{\mu}\right)_{\lambda-1}, \\ H_\lambda &= H_{\lambda-1} \frac{\cos \phi_\lambda}{\cos \phi'_\lambda} + k'_\lambda G_\lambda, \end{aligned} \right\} \quad \dots \quad (16)$$

where $k' = k\epsilon$, and are the same as (7) and (9) above with G written for $-\eta$ and H for $\mu d\psi$.

Also

$$\frac{(EH - FG)_\lambda}{(EH - FG)_1} = \frac{\cos \phi'_1 \cdot \cos \phi_\lambda}{\cos \phi_1 \cdot \cos \phi'_\lambda},$$

or

$$(EH - FG)_\lambda \frac{\cos \phi'_\lambda}{\cos \phi_\lambda} = \text{constant for all values of } \lambda.$$

As regards initial values, the equation of refraction gives

$$q'_1 = \frac{p'_1}{1 + k_1 p'_1},$$

and hence

$$E_1 = 0, \quad F_1 = 1, \quad G_1 = 1, \quad H_1 = k'_1.$$

Hence replacing q' , p' by their values in terms of the original q , p , (15) yields

$$\left(\frac{q_n}{\mu_n} - \frac{G_n}{H_n} \cdot \frac{\cos \phi'_n}{\cos \phi_n}\right)\left(\frac{p_1}{\mu_0} + \frac{F_n}{H_n} \cdot \frac{\cos \phi_1}{\cos \phi'_1}\right) = -\frac{1}{H_n^2} \dots \quad (17)$$

If we reverse the order, and, instead of expressing q'_λ in terms of p'_1 as in (13), express p'_λ in terms of q_n , putting

$$p'_\lambda = \frac{E'_\lambda + G'_\lambda q'_n}{F'_\lambda - H'_\lambda q'_n},$$

we obtain in a similar manner relations between the G 's and H 's like (8) and (10). $H'_1 = H_n$, and we get the following equation instead of (17):

$$\left(q_n - \frac{F'_1 \cos \phi'_n}{H_n \cos \phi_n} \right) \left(\frac{p_1}{\mu_0} + \frac{G'_1 \cos \phi_1}{H_n \cos \phi_1} \right) = - \frac{1}{H_n^2}. \quad (18)$$

II. *Formulæ for the Secondary Focal Distances.*

The following is an alternative discussion of the case of the sagittal section:—

Taking the optic axis as axis of x ,

let y_0, z_0 be coordinates of the object point P,

y_n, z_n „ „ „ „ secondary focus Q,

Y_1, Z_1 „ „ „ „ point of incidence,

Y_n, Z_n „ „ „ „ „ emergence,

M_0, N_0 „ „ direction cosines of the incident ray,

M_n, N_n „ „ „ „ emergent ray,

u „ „ the distance of the object point from the lens
along the ray,

v „ „ the distance of the secondary focus from the lens
along the ray,

ν „ „ the magnification.

When the ray is in an axial plane, conjugate line elements perpendicular to the ray in the sagittal section are proportional to their distances from the optic axis. For a ray

not in an axial plane, we define ν by $\nu = \sqrt{\frac{y_n^2 + z_n^2}{y_0^2 + z_0^2}}$.

The salient characteristic of a pair of secondary foci for a single surface is that the line joining them passes through the centre. Hence in a coaxial system all successive secondary foci lie in the axial plane through the object point. The equation of an axial plane through P is $yz_0 = zy_0$. Expressing the fact that Q lies on this plane, we have

$$\frac{y_n}{y_0} = \frac{z_n}{z_0} = \sqrt{\frac{y_n^2 + z_n^2}{y_0^2 + z_0^2}} = \nu.$$

Also

$$\begin{aligned} y_1 - Y_1 &= M_0 u, & y_n - Y_n &= M_n v, \\ z_1 - Z_1 &= N_0 u, & z_n - Z_n &= N_n v. \end{aligned}$$

Thus, if v is given, we have six equations connecting the six quantities y_0, z_0, y_n, z_n, u, v . By straightforward elimination we can get rid of y_0, z_0, y_n, z_n , and obtain two equations in u and v , whence

$$u(M_0N_n - N_0M_n) = -(Y_1N_n - Z_1M_n) + \frac{1}{v}(Y_nN_n - Z_nM_n), \quad (19)$$

$$v(M_0N_n - N_0M_n) = (Y_nN_0 - Z_nM_0) - v(Y_1N_0 - Z_1M_0). \quad (20)$$

In this form the rays are not applicable to rays in the plane $z=0$. The ratios of the coefficients must be reduced to a form which does not become indeterminate in that case.

Now, by the well-known law of refraction, we have

$$\mu_\lambda M_\lambda - \mu_{\lambda-1} M_{\lambda-1} = -k_\lambda Y_\lambda$$

and evidently

$$Y_\lambda - Y_{\lambda-1} = \frac{t_{\lambda-1}}{\mu_{\lambda-1}} (\mu M)_{\lambda-1}.$$

Two similar relations connect Z and N .

Suppose C_n, K_n to be final values given by the sequence equations

$$K_\lambda - K_{\lambda-1} = k_\lambda C_\lambda$$

$$C_\lambda - C_{\lambda-1} = -\left(\frac{t}{\mu} K\right)_{\lambda-1},$$

for initial values $C_0=1, K_0=0$.

Then by (4)

$$\mu_n M_n = -Y_1 K_n, \quad Y_n = Y_1 C_n; \quad \mu_n N_n = -Z_1 K_n, \quad Z_n = Z_1 C_n;$$

$$\therefore \mu_n (M_0 N_n - N_0 M_n) = K_n (Y_1 N_0 - M_0 Z_1),$$

$$Y_n N_0 - Z_n M_0 = C_n (Y_1 N_0 - M_0 Z_1).$$

Hence, cutting out the factor $Y_1 N_0 - Z_1 M_0$ in each term, (20) becomes

$$\frac{v}{\mu_n} = \frac{C_n - v}{K_n}.$$

Similarly, supposing C'_1 and $K'_1 = K_n$ to be values given by

$$C'_{\lambda-1} - C'_\lambda = \left(\frac{t}{\mu} K'\right)_{\lambda-1},$$

$$K'_{\lambda-1} - K'_\lambda = -k_\lambda C'_\lambda,$$

starting with $C'_n=1, K'_n=0$, and working backwards, then we find values for the first two coefficients of (19) containing $Y_n N_n - Z_n M_n$ as a factor; and on cutting out this factor the

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equation reduces to

$$\frac{u_1}{\mu_0} = -\frac{C'_1}{K_n} + \frac{1}{\nu K_n}.$$

The second method adopted above becomes much simpler in the case of the secondary foci. The equation of refraction is

$$\frac{\mu_\lambda}{v_\lambda} - \frac{\mu_{\lambda-1}}{u_\lambda} = k_\lambda.$$

By putting in turn

$$v_\lambda = \frac{A_\lambda + C_\lambda u_1}{B_\lambda + K_\lambda u_1} \quad \text{and} \quad u_\lambda = \frac{A'_\lambda + C'_\lambda v_n}{B'_\lambda + K'_\lambda v_n},$$

and equating coefficients in two expressions as before in the case of the primary foci, we arrive at relations between the coefficients (A, K and C, K') of exactly the same form as in the paraxial case, the only difference being that the paraxial t and k are replaced by those defined above under "*Nomenclature.*"

LXXXV. *A Consequence of the Theory of M. Louis de Broglie.*
(Phil. Mag., February 1924, p. 446.)

M. DE BROGLIE'S formula :

$$h\nu = \frac{m_0 c^2}{\sqrt{1-\beta^2}}$$

gives

$$\beta = \sqrt{1 - \frac{m_0^2 c^4}{h^2 \nu^2}},$$

or

$$v = c \sqrt{1 - \frac{m_0^2 c^4}{h^2 \nu^2}}.$$

M. de Broglie estimates m_0 as being of the order of 10^{-50} gr. Let us take a vibrator with a period of $T = 726\frac{2}{3}$ sec. If we put in de Broglie's formula $m_0 = 10^{-50}$, $c = 3 \cdot 10^{10}$, $h = 6 \cdot 54 \cdot 10^{-27}$, and $\nu = \frac{1}{T} = \frac{1}{726\frac{2}{3}} = \frac{3}{2180}$, the result will be
 $v = 0.$

The velocity of the waves is zero! Our vibrator cannot emit electromagnetic waves! Likewise the inductive effect in a transformer of an alternating current with a period of $T = 726\frac{2}{3}$ sec. must be equal to zero. It would be interesting to examine the question experimentally.

Dorpat,
27th February, 1924.

WILHELM ANDERSON.

LXXXVI. *The Arc Spectrum of Phosphorus.*

By M. O. SALTMARSH, B.A., F.Inst.P.*

Introduction.

THE wave-lengths of a large number of lines in the spectrum of phosphorus, produced under a variety of conditions, have been measured by Geuter † over the range $\lambda 5728$ – $\lambda 2390$ A.U. The only lines which occurred in the spectrum of a carbon arc to which a compound of phosphorus had been added were two pairs in the ultra-violet between $\lambda 2555$ and $\lambda 2534$. These were also produced in a discharge through phosphorus vapour in a vacuum tube. They are recorded by De Gramont ‡ as being the persistent rays of phosphorus. Three triplets and several pairs of constant frequency difference have been noted by Paulson § in the spectrum of phosphorus in the region from $\lambda 5500$ to $\lambda 3348$. The radiation and ionization potentials of phosphorus have been measured by Foote and Mohler ||.

Phosphorus is an element of group V of the periodic table, and no series relationships have yet been worked out for any of these elements. Multiplets have recently been found in the spectrum of vanadium ¶. The investigation of the spectrum of phosphorus was therefore undertaken with a view to separating the arc and various enhanced spectra from each other and to determining regularities and possibly series relationships in each. The present paper deals with the arc spectrum.

Experimental Procedure.

With the exception of possible lines in the infra-red, in which region no investigation has been made, the arc spectrum of phosphorus lies completely in the ultra-violet beginning at $\lambda 2555$.

The spectrum was produced in two ways : (1) by feeding phosphorus pentoxide into a carbon or a copper arc, and (2) by passing a discharge from an induction coil through a Geissler tube containing yellow phosphorus and hydrogen at a low pressure. The tube was provided with a quartz or fluorite window, and was used in the end-on position : the phosphorus was introduced through a side tube having a

* Communicated by Prof. A. Fowler, F.R.S.

† Geuter, *Zeit. Wiss. Phot.* v. p. 1 (1907).‡ De Gramont, *Comptes Rendus*, cxlvi. p. 1260 (1908).§ Paulson, *Ann. d. Phys.* xlv. p. 419 (1914).|| Foote & Mohler, *Phys. Rev.* xv. (1920).¶ Meggers, *Jour. Wash. Acad.* Aug. 1923; and Laporte, *Die Naturwissenschaften*, Sept. 1923.

ground-glass stopper. It was found unnecessary to heat the tube in order to bring out the phosphorus lines.

Four different spectrographs were employed for the various regions investigated :—

1. For wave-lengths greater than λ 2200, a quartz Littrow spectrograph giving a linear dispersion of 2.8 Å. to the millimetre at λ 2530.
2. For wave-lengths between λ 2200 and λ 2100, a Hilger quartz spectrograph having a linear dispersion of 4.7 Å. to the millimetre in that region.
3. For wave-lengths between λ 2100 and λ 1850, a Hilger quartz spectrograph having a linear dispersion of 12.3 Å. to the millimetre at λ 2030, and 9.4 Å. to the millimetre at λ 1890.
4. For wave-lengths shorter than λ 1850, a Hilger vacuum grating spectrograph giving an approximately normal spectrum in the first order with a linear depression of 17.2 Å. to the millimetre.

The wave-lengths of phosphorus lines greater than λ 1850 were measured on plates taken with an arc fed with phosphorus pentoxide as source.

Comparison Spectra.

The wave-lengths of the phosphorus lines are given in international angstroms reduced to vacuum, and for the various regions it was necessary to employ different comparison spectra.

Between λ 2550 and λ 2300 the iron arc was used for comparison, the wave-lengths being those given in Burns' tables. In this region the measurements are probably accurate to 0.05 Å.

In the region λ 2300 to λ 2100 the copper arc was used for comparison, the wave-lengths being those given by Hasbach*. The accuracy of the measurements in this region is probably as great as that of measurements between λ 2550 and λ 2300.

Between λ 2100 and λ 1850 a silver spark was employed, and the wave-lengths used were those given by Eder†. The possible error is about 0.05 Å. for lines in the region near λ 1850, and rather greater than that for lines near λ 2030.

The spectrograms taken with the vacuum spectrograph were treated as normal and the wave-lengths calculated from two known lines which appeared on the plate.

* Hasbach, *Zeitsch. Wiss. Phot.* p. 399 (1914).

† Eder, *Zeitsch. Wiss. Phot.* xiv. (1915).

namely a carbon line at $\lambda 1930.61$ * and a hydrogen line at $\lambda 1553.3$ †. The possible error in the values of these lines is about 0.3 Å.

Description of Spectra.

The arc spectrum of phosphorus from $\lambda 2550$ to $\lambda 1672$ probably consists of 35 lines, only four of which have been previously recorded. With the exception of the two faint lines $\lambda 1864.1$ and $\lambda 1856.6$, all the lines of wave-length greater than $\lambda 1850$ have been produced in two entirely different ways, thus establishing that they are due to phosphorus. They appear in the spectrum when P_2O_5 is added to a carbon or a copper arc, and also in the spectrum of a discharge through a tube containing yellow phosphorus and hydrogen at a low pressure. In the arc they are the only phosphorus lines which appear, but in the vacuum-tube discharge they may be the only phosphorus lines, or there may be others present as well, if the intensity of the discharge is great enough or the pressure of the hydrogen sufficiently low.

In the Schumann region an arc fed with a compound of phosphorus was found to be unsuitable as a source: consequently in this region the lines have been produced in only one way. Those which have been assigned to phosphorus are the additional lines which appear when yellow phosphorus is added to the tube. This assignment is probably correct, because in the region where two different sources could be used, the introduction of phosphorus into the vacuum tube was found to result only in extra lines due to phosphorus and none due to impurities. It must, however, be stated that the origin of lines of wave-lengths shorter than $\lambda 1850$ is not definitely established.

Although the line of shortest wave-length belonging to phosphorus that has been observed is $\lambda 1671.5$, the plates in some cases showed lines of the hydrogen secondary spectrum down to $\lambda 1333$; but beyond 1671.5 no phosphorus lines could be observed among the strong groups of hydrogen lines. In order to determine to which spectrum of phosphorus the lines belonged, photographs were taken with different strengths of discharge, and the change in intensity of the lines observed. The lines which occur in the arc, can be produced alone of all the phosphorus lines by using an uncondensed discharge through phosphorus vapour in a vacuum tube containing also hydrogen at a comparatively high pressure, or by using a condensed discharge and hydrogen at a still higher pressure, so that H_α and H_β are

* Simeon, Proc. Roy. Soc. A, cii. (1922).

† Lyman, 'Spectroscopy of the Extreme Ultra-Violet,' p. 111.

very broad lines. When the pressure of the hydrogen is reduced and the intensity of the discharge through the phosphorus vapour is consequently increased, the arc lines become more intense at first and a few additional phosphorus lines make their appearance. With still further reduction of pressure of the hydrogen the arc lines decrease in intensity and become diffuse, while the new phosphorus lines brighten and very many more appear. Hence it is concluded that the lines which decrease in intensity in this manner belong to the arc spectrum, while the others are enhanced lines.

Table I. gives a list of the wave-lengths in international units reduced to vacuum, the wave-numbers in vacuum, the

TABLE I.

Wave-length.	Wave-number.	Intensity.	Character.	Source.
2555.68	39128.5	8	s*	Arc and vacuum tube.
2554.02	39154.0	9	s	" " "
2536.38	39426.3	10	s	" " "
2534.75	39451.6	8	s	" " "
2154.77	46408.7	7	s	" " "
2153.63	46433.2	6	s	" " "
2149.81	46515.7	8	s	" " "
2136.79	46799.2	8	s	" " "
2136.10	46814.2	6	s	" " "
2034.02	49163.7	7	s	" " "
2032.98	49188.9	6	s	" " "
2024.98	49383.2	6	s	" " "
2023.98	49407.6	7	s	" " "
1957.69	52419.4	1	s	" " "
1905.59	52477.2	0	s	" " "
1864.1	53645	1	s	Vacuum tube only.
1859.36	53782.0	6	s	Arc and vacuum tube.
1858.85	53796.7	8	s	" " "
1856.6	53862	0	d*	Vacuum tube only.
1851.11	54021.6	6	s	Arc and vacuum tube.
1846.8	54148	7	s	Vacuum tube only.
1844.0	54230	1	d	" " "
1834.5	54511	4	s	" " "
1825.9	54768	0.5	d	" " "
1829.3	54936	1	d	" " "
1787.5	55944	6.5	s	" " "
1782.7	56095	7	s	" " "
1774.8	56344	7	s	" " "
1719.0	58173	1.5	d	" " "
1693.8	59039	4.5	s	" " "
1689.1	59203	0.5	s	" " "
1685.8	59319	5	s	" " "
1679.5	59542	1.5	s	" " "
1674.4	59723	1.5	s	" " "
1671.5	59827	3	dv*	" " "

* s Means sharp.

d " diffuse.

dv " diffuse towards shorter wave-lengths.

intensities and character of the lines, and the sources in the spectrum of which the lines were observed. The intensities can be taken as having only local values, on account of the fact that many of the different groups of lines were either photographed on different plates, or on the same plate, the sensitiveness of which varied considerably within the range used.

Regularities in the Spectrum.

It will be seen that the spectrum consists of isolated groups of lines.

The group of four lines between $\lambda 2556$ and $\lambda 2535$ were found by De Gramont* to be the "raies ultimes" for phosphorus. For many elements the "raies ultimes" are the first lines of one of the series and also the lines corresponding to the radiation potential, which for phosphorus is $5.80 \pm .1$ volt†.

The extreme limits 5.70 volt and 5.90 volt of the radiation potential correspond to the spectral lines $\lambda 2165$ and $\lambda 2092$, which therefore do not agree with the wave-lengths of the "raies ultimes". But the group of five lines of wave-lengths $\lambda 2154.77$, $\lambda 2153.63$, $\lambda 2149.81$, $\lambda 2136.79$, $\lambda 2136.10$ in the phosphorus arc spectrum lie well within these limits, so that any one of them might be a resonance line. This group of lines is isolated, the interval between $\lambda 2154.77$ and the next line of longer wave-length being 380 A.U., and that between $\lambda 2136.10$ and the next line of shorter wave-length 102 A.U. The vapour of phosphorus is polyatomic at the temperature at which the radiation potential was measured, and in such a case it is not clear whether the radiation comes from excited molecules or from excited atoms which have previously been formed by dissociation of the molecule. If it comes from the former, the agreement of the resonance wave-length of phosphorus with that of a line in the arc spectrum is merely fortuitous. It is found, however, that in the case of hydrogen, which is diatomic, the first radiation potential, 10.2 volts, agrees with $\lambda 1215.7$, the first line of the Lyman series, and it is attributed by Horton and Davies‡ to atomic excitation. The case of phosphorus may be analogous.

The thirty-five lines recorded as belonging to the phosphorus arc spectrum are connected together by systems of

* De Gramont, *loc. cit.*

† Foote & Mohler, *loc. cit.*

‡ Horton & Davies, *Phil. Mag.* Nov. p. 873 (1923).

doublets of constant frequency differences, every one of the lines being involved. These are recorded in Table II. together with the intensities of the lines. It will be observed

TABLE II.

Wave-length.	Intensity.	Frequency difference.	Wave-length.	Intensity.	Frequency difference.
2555.68 } 2554.02 } 2536.38 } 2534.75 } 2154.77 } 2153.63 } 2034.02 } 2032.98 } 2024.98 } 2023.98 }	8 9 10 8 7 6 7 6 6 7	25.4 25.4 24.5 25.2 24.4	2154.77 * } 2024.98 * } 2153.63 * } 2023.98 * } 1774.8 } 1685.8 * }	7 6 6 7 7 5	2974.5 2974.4 2975
2149.81 } 2136.79 } 1856.6 } 1846.8 } 1844.0 } 1834.5 } 1693.8 } 1685.8 } 1679.5 } 1671.5 }	8 8 0 7 1 4 4.5 5 1.5 3	283.5 286 281 280 285	2555.68 * } 2154.77 * } 2554.02 * } 2153.63 * } 2149.81 * } 1858.85 }	8 7 9 6 8 8	7280.2 7279.2 7281.0
2534.75 * } 2136.79 * } 2153.63 * } 1859.36 } 2149.81 * } 1856.6 * } 2136.79 * } 1846.8 * } 1905.59 } 1671.5 * }	8 8 6 6 8 0 8 7 0 3	7347.6 7348.8 7346 7349 7350	2023.98 * } 1859.36 * } 1858.85 * } 1719.0 } 1820.3 } 1685.8 * }	7 6 8 1.5 1 5	4374.4 4376 4383
2555.68 * } 2536.38 * } 2554.02 * } 2534.75 * } 2149.81 * } 2136.10 }	8 10 9 8 8 6	297.8 297.6 298.6	2154.77 * } 2136.10 * } 1787.5 * } 1774.8 * } 1685.8 * } 1674.4 }	7 6 6.5 7 5 1.5	405.6 400 404
			1856.6 * } 1851.11 } 1825.9 * } 1820.3 * } 1693.8 * } 1689.1 }	0 6 0.5 1 4.5 0.5	160 168 164
			2136.10 * } 2034.02 * } 1907.69 } 1825.9 }	6 7 1 0.5	2349.4 2349
			1864.1 * } 1858.85 * } 1787.5 } 1782.7 }	1 8 6.5 7	152 151

* Used before.

that in some cases the frequency differences differ among themselves by several units, but in all cases they are within the limits of experimental error. In the Schumann region the possible error of measurement was estimated to be 0.3 Å., and at λ 1850 the corresponding possible error in the wave-number is 9 units and at λ 1671 it is 11 units. At λ 2556 a difference of 0.04 in the wave-length makes a difference of 0.6 in the wave-number. In spite of the variation between some of the frequency differences, it seemed worth while to record them, since the range of wave-number within which the lines lie is comparatively great for so small a number of lines, and the approximate agreement is more significant than if the lines were close together. They serve, at any rate, to show that the arc spectrum of phosphorus almost certainly consists of doublets, and thus falls into line with elements obeying the Sommerfeld-Kossel displacement law, which requires the arc spectrum of phosphorus to contain series of doublets.

The frequencies of all the lines up to λ 1858.85, with the exception of the three lines λ 1907.69, λ 1905.59, λ 1864.1, which are of low intensity, can be expressed by means of nine terms. These lines are among those which are known definitely to belong to the arc spectrum of phosphorus, and if the terms are a , b , c , d , e , and α , β , γ , δ , the lines are as follows:—

TABLE III.

λ 2555.68 (8) $a-\alpha$	λ 2136.10 (6) $\gamma-b$
λ 2554.02 (9) $\beta-a$	λ 2034.02 (7) $a-d$
λ 2536.38 (10) $a-b$	λ 2032.98 (6) $\beta-d$
λ 2534.75 (8) $\beta-b$	λ 2024.98 (6) $a-e$
λ 2154.77 (7) $a-c$	λ 2023.98 (7) $\beta-e$
λ 2153.63 (6) $\beta-c$	λ 1859.36 (6) $\delta-c$
λ 2149.31 (8) $\gamma-a$	λ 1858.85 (8) $\gamma-c$
λ 2136.79 (8) $\delta-b$	

Some of these terms can be identified by arranging the lines in multidoublets, similar to those discovered by Catalán* in the arc spectrum of scandium.

The group at about λ 2550 can be arranged as a multidoublet of the PP' type with the expected relative intensities as follows:—

* Catalán, *Anal. d. Soc. Esp. Fis. y Quim.* xx. p. 606 (1922).

λ .	ν .	Intensity.	Designation.
2555.68	39128.5	8	$P_1' P_2$
2554.02	39154.0	9	$P_2' P_2$
2536.38	39426.0	10	$P_1' P_1$
2534.75	39451.6	8	$P_2' P_1$

The scheme of the multidoublet is

(8)		(9)
39451.6	297.6	39154.0
25.4		25.4
(10)		(8)
39426.3	297.8	39128.5.

Hence $P_2 - P_1 = 297.7$ and $a = P_2$, $b = P_1$; also $P_2' - P_1' = 25.4$ and $\beta = P_2'$, $\alpha = P_1'$. The former separation occurs once more and the latter three times more.

If the lines are correctly represented in Table III., there is a multidoublet of the DP type among the $\lambda 2140$ group as follows:—

λ .	ν .	Intensity.	Designation.
2149.81	46515.7	8	$D_2 P_2$
2136.79	46799.2	8	$D_1 P_1$
2136.10	46814.2	6	$D_2 P_1$

(6)		(8)
46814.2	298.5	46515.7
15.0		
(8)		
46799.2		

Hence $D_2 - D_1 = 15.0$ and $\gamma = D_2$, $\delta = D_1$. The separation 15.0 occurs once again at $\lambda 1858$. The group of four lines near $\lambda 2030$ is very like a multidoublet of the PP' type, except that the intensities are in the opposite order

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to that expected. It can be represented as follows if $P_1'' > P_2''$:—

λ .	ν .	Intensity.	Designation.
2034.02	49163.7	7	$P_1' P_1''$
2032.98	49188.9	6	$P_2' P_1''$
2024.98	49383.2	6	$P_1' P_2''$
2023.98	49407.6	7	$P_2' P_2''$

(7)		(6)
49407.6	218.7	49188.9
24.4		25.2
(6)		(7)
49383.2	219.5	49163.7

Hence $P_1'' - P_2'' = 219.1$ and $d = P_1''$, $e = P_2''$. The remaining four lines in Table III. have only one term, common to them all, which is not identified. This classification of the lines is not completely satisfactory, but it tends to confirm the doublet nature of the series to be expected in the arc spectrum of phosphorus.

Summary.

1. The arc spectrum of phosphorus has been investigated from the visible region up to λ 1671. The whole spectrum lies in the ultra-violet beyond λ 2555, and probably consists of thirty-five lines within this range.

2. A group of five close lines, which is widely separated from neighbours, has been found such that any one of the lines agrees in wave-length with that calculated from the radiation potential.

3. The frequencies of all the lines are connected by systems of doublets of constant frequency differences, and thus the arc spectrum of phosphorus probably obeys the Sommerfeld-Kossel displacement law.

4. The frequencies of fifteen of the strongest lines can be expressed by means of nine terms, and some of these lines can be arranged as multidoublets.

The work described in this paper has been carried out under the direction of Professor A. Fowler, and the author wishes to express her gratitude to him for his generous help and interest.

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LXXXVII. *The Rate of Heat Transmission from the Working Fluid in an Internal Combustion Engine.* By Prof. A. H. GIBSON, D.Sc.*

1. **T**HE rate of heat transmission from the hot gases contained in a metal chamber to the cool walls depends upon the temperature difference, the density, the turbulence, and to some extent on the dimensions of the chamber.

In experiments on cooling following explosion in an explosion vessel the turbulence is small, and heat transmission is mainly due to radiation. Under these conditions, experiments by Sir Dugald Clerk † indicate that the rate of heat transmission is proportional to ϕ^n , where ϕ is the temperature difference, and where, between the limits of 1100°C. and 1450°C. , n has a mean value of $2\cdot8$. Hopkinson's results ‡ between 1300°C. and 1760°C. show $n=2\cdot45$, and Petavel's § experiments between 320°C. and 2200°C. show $n=2\cdot35$. In the experiments of Clerk and Hopkinson the density was atmospheric. In those of Petavel it was considerably higher (up to 75 atmospheres). Petavel's experiments at different densities indicate that the heat transmission is proportional to ρ^n at a given temperature, where $n=3\cdot5$ at 1760°C. Bairstow and Alexander's || experiments at densities from 1 to 3 atmospheres indicate a value of $n=3\cdot5$ at 1400°C. , but this value is appreciably reduced at higher temperatures.

On the other hand, when, as in an engine in operation, the transference of heat from the gas to the metal surfaces is largely dependent on the velocity of the gas, the heat-loss is more nearly proportional to the density. Thus in his gas-engine experiments Hopkinson ¶ found that the total heat-loss, including that after release, was proportional to $\rho^{\frac{2}{3}}$, while from piston temperature measurements he found it proportional to $\rho^{\frac{2}{3}}$.

2. A knowledge of the rate of heat transmission under the conditions holding during the working cycle of an internal combustion engine would be of great value in enabling the rate of heat-flow into the exposed surfaces and the magnitude of the surface fluctuations of temperature to be determined.

* Communicated by the Author.

† Clerk, 'The Petrol and Gas Engine,' vol. i. p. 204 (1909).

‡ Proc. Roy. Soc. A, 1906, p. 387.

§ Clerk, 'The Petrol and Gas Engine,' vol. i. p. 166.

|| Proc. Roy. Soc. A, 1905.

¶ Proc. Inst. C. E. clxxvi. pt. ii. (1908-9)

Its direct experimental determination is one of much difficulty, and no definite values have hitherto been available, especially at the temperatures and with the degrees of turbulence which obtains in a high-speed petrol engine in operation. Some idea of its magnitude may be deduced from the valuable data obtained by Sir Dugald Clerk* in his experiments on the cooling of the fluid in the cylinder of a gas-engine. These measurements, however, refer not to the working stroke, but to the succeeding strokes, in which the turbulence is less by some unknown amount than in the normal working stroke.

Its value under operating conditions may be deduced indirectly (*a*) from measurements of the temperature gradient along a radius of the piston of the engine, or (*b*) from measurements of the cyclical fluctuation of surface temperature of the piston or walls of the combustion chamber; and the present paper is devoted to an examination of such measurements with a view of obtaining a reasonably close approximation to this value.

3. Some few measurements of piston temperatures in the cylinders of gas-engines are available, notably by Hopkinson on a cast-iron piston 11.5 in. diameter by 1.5 in. thick, at 180 revs. per minute; by Coker and Scoble† on a cast-iron piston 7 in. diameter by $\frac{3}{8}$ in. thick, at 200 and 240 revs. per minute; and by Jardine and Jehle‡ on two aluminium pistons, 5 in. diameter and respectively $\frac{1}{4}$ in. and $\frac{3}{8}$ in. thick, in a petrol-engine cylinder at 800 r.p.m. In addition to these, the author has carried out experiments on a number of aluminium and cast-iron pistons of various thicknesses, 100 mm. diameter, in a petrol-engine cylinder at speeds of 1800 and 2000 r.p.m. § The data thus cover a wide range of operating conditions.

The amount of available data regarding the magnitude of the fluctuations of surface temperature is not large. A number of experimental determinations are, however, given in the paper by Messrs. Coker and Scoble ||, and these have been used as a check on the values obtained from the piston temperature measurements.

4. If the temperature gradient across the face of a piston is known, the rate of reception of heat "*h*" per unit area of the face, or rather the difference between the rate at which

* Proc. Roy. Soc. A, lxxvii. p. 499 (1906).

† Proc. Inst. C. E. cxvii. pt. ii. (1913-14).

‡ American Society of Automotive Engineers (May 1921).

§ Advisory Committee for Aeronautics. L.A.S.C. Reports, No. 13 (May 1918).

|| *Loc. cit.*

heat is being received by the working face and dissipated at the lower face of the piston crown, is given very approximately by

$$h = \frac{4kt\theta}{a^2 + t^2}, \quad \dots \quad (1)$$

where θ is the difference of temperature between the centre and a point at radius a ,

t is the thickness of the piston crown,

k is the conductivity of the material,

If $(\theta_1 - \theta_2)$ be the difference of temperature at two radii a_1 and a_2 , this becomes

$$h = \frac{4kt(\theta_1 - \theta_2)}{(a_2^2 - a_1^2)}. \quad \dots \quad (2)$$

In a piston in which the thickness of the crown varies with the radius, if over any portion of the crown between radii a_1 and a_2 the thickness is proportional to the radius so that $t = Ca$, we have

$$\begin{aligned} \delta\theta &= \frac{h(a_2^2 - a_1^2)}{4kt}, \\ &= h \times \frac{2a \delta a}{4kt}, \\ &= h \frac{\delta a}{2kC}; \\ \therefore \theta_1 - \theta_2 &= \frac{h}{2kC} \int_{a_1}^{a_2} da, \\ &= \frac{h(a_2 - a_1)}{2kC}. \quad \dots \quad (3) \end{aligned}$$

In a number of the author's pistons (viz. A, A', B, and C, Table I.) this condition is satisfied over the range of radii 0.5 in. to 1.0 in. (1.27 cm. to 2.54 cm.), the value of C being 0.31.

5. *Cyclical Fluctuations of Surface Temperature.*—On the assumptions that the working fluid in contact with the metal has a cyclical fluctuation of temperature of $\pm A^\circ \text{C}$; that the heat transmission from the gas to the metal is directly proportional to their difference of temperature; and that this produces a simple harmonic fluctuation of temperature in the metal: it may be shown that in the case

of a large flat surface the magnitude "*a*" of the fluctuation of surface temperature is given by

$$a = \frac{Ae'}{\sqrt{\pi n \rho s k + (e' + \sqrt{\pi n \rho s k})^2}}, \quad \dots \quad (4)$$

where *n* is the number of explosions per second,

ρ is the density of the metal,

s is the specific heat of the metal,

k is the thermal conductivity of the metal,

e' is the receptivity, i. e. the heat transmitted from the gas to the surface per second per unit area per degree difference of temperature between metal and gas.

If *e'* is relatively small, as is shown later to be the case,

$$a = \frac{Ae'}{\sqrt{2\pi n \rho s k}} \text{ approximately. } \dots \quad (5)$$

So that

$$\frac{a}{A} \propto \frac{1}{\sqrt{n}} \text{ for a piston of given material,}$$

$$\frac{a}{A} \propto \frac{1}{\sqrt{\rho s k}} \text{ for pistons of different materials operating at the same speeds of rotation.}$$

The assumption that *e'* in the above formulæ is a constant is, however, very far from being true. Actually, Sir Dugald Clerk's experimental results indicate that under the conditions obtaining in a gas-engine, the heat transmission "*h*" per unit area per second is more nearly proportional to *φ*", where *φ* is the difference of temperature between gas and metal, and where *n* is very nearly equal to 2*. If *n* be assumed equal to 2 for convenience in calculation, the results will be very much nearer representing the true state of affairs than those deduced on the assumption that *n*=1, and if *n*=2 it may be shown that the formula corresponding to (5) is

$$a = \frac{e\{(T_1 - \theta_0)^2 - (T_2 - \theta_0)^2\}}{2\sqrt{2\pi n \rho s k}}, \quad \dots \quad (6)$$

where *T*₁ is the maximum temperature of the gas during the cycle,

*T*₂ is the minimum temperature of the gas during the cycle,

*θ*₀ is the mean temperature of the surface during cycle,

*eφ*²=*h*=heat transmitted per unit area per second from gas to surface.

* See Section 9.

6. The essential data from the author's pistons, under full-load conditions, are given in Table I.

TABLE I.

Line.	Piston.	Temperature ° C. at					Mean wall temp. ° C.
		Centre.	·5 in. rad.	1·0 in. rad.	1·5 in. rad.	Edge.	
1 ...	A	194°	197°	167°	149°	139°	112°
2 ...	A'	235	240	210	187	175	119
3 ...	B	198	199	169	152	140	114
4 ...	C	205	210	183	160	147	122
5 ...	G	215	229	201	170	148	120
6 ...	Cast iron ..	409	419	366	283	184	120

An examination of the drawings of the aluminium pistons shows that at the radius 1·5 in. the effect of the large fillet joining the crown to the skirt has an appreciable effect on increasing the thickness. Over the range of radii from 0·5 in. to 1·0 in., however, the thickness is constant in piston G, while in pistons A, A', B, and C it is sensibly proportional to the radius. Taking the average value of the gradient over this range of radius in these four pistons, calculations based on equation (3) give $h = 5·56$ C.G.S. units, while for piston G, $h = 5·75$ C.G.S. units. The corresponding value of h for the cast-iron piston is 1·60. The values of h deduced from these experiments and from those by other observers are given in Table II.

TABLE II.

Authority.	Type of Engine.	h (C.G.S. units.)	e (C.G.S. units.)
HOPKINSON ...	Gas-engine: 11·5 in. C.I. piston; 180 r.p.m.; stroke 21 in. (Normal mixtures).....	1·43	$3·9 \times 10^{-6}$
COKER	Gas - engine: 7 in. C.I. piston; 200 r.p.m.; stroke 15 in. (Normal mixtures).....	1·16	$3·4 \times 10^{-6}$
JARDINE & JENLE.	Aero-engine: 5 in. aluminium piston; 800 r.p.m.; stroke 7 in.		
	Piston ·25 in. thick.....	4·15	$9·0 \times 10^{-6}$
	" ·375 in. "	4·05	$8·8 \times 10^{-6}$
AUTHOR	Petrol-engine: 1800 r.p.m; stroke 140 mm.		
	Aluminium pistons A, A', B, C, 100 mm. diam.	mean 5·56	$11·0 \times 10^{-6}$
	Aluminium piston G, 100 mm. diam.....	5·75	$11·0 \times 10^{-6}$
	Cast - iron piston, 100 mm. diam.	1·60	$5·1 \times 10^{-6}$

In calculating these values, k has been taken as 0.11 for cast iron at 200° C., 0.102 at 350° C.; 0.38 for aluminium alloy at 200° C. and 0.39 at 300° C.*

The value of h deduced from equations (1), (2), or (3) represents the mean rate of heat inflow during the cycle, and the determination of e from h necessitates a knowledge of the mean square of the temperature difference between gas and surface on a time base during the cycle.

On the usual assumption that the fluctuation of gas temperature is simple harmonic, it may be shown that this mean square is equal to †

$$\left\{ \frac{T_1 - T_2}{2} - \theta_0 \right\}^2 + \frac{\{T_1 - T_2\}^2}{8} \dots \dots (9)$$

Calling this ϕ^2 , we then have $h = e\phi^2$. An examination of Coker's measurements of gas temperature throughout the cycle shows, however, that the assumption as to simple harmonic fluctuation gives results which are very far from the truth. Thus, taking the difference of temperature between gas and piston at crank angles of 30°, 90°, etc. in test G ‡ of Coker's paper, and calculating the mean of the squares of the differences throughout the cycle gives 335,000. In this test $T_1 = 2040^\circ$ C. approx.; $T_2 = 217^\circ$; and the mean temperature θ_0 of the piston between the points of measurement is 196°. Inserting these values in equation (7) makes ϕ^2 equal to 1,291,000, or 3.85 times its true value as deduced from the temperature curve. A similar examination of all the test results in this latter paper shows that this ratio varies between 3.85 and 4.09 in the different experiments, the maximum variation from the value 4.0 being less than 4 per cent. It is probable, therefore, that without serious error it may be assumed that under normal conditions of operation in such engines the value of ϕ^2 is given by

$$\frac{1}{4} \left\{ \left(\frac{T_1 + T_2}{2} - \theta_0 \right)^2 + \frac{(T_1 - T_2)^2}{8} \right\},$$

and that e equals h divided by this expression.

In Coker's full-load tests the following are the approximate values of the temperatures: $T = 2120^\circ$ C., $T_2 = 270^\circ$, $\theta_0 = 230^\circ$; while the value of h , deduced from the mean temperature across the piston, is 1.16 C.G.S. units. The

* These values were measured for the materials from which the 100-mm. pistons were made.

† See Appendix.

‡ Proc. Inst. C. E. pt. ii. p. 42 (1913-14).

mean value of ϕ^2 is 340,000, making the mean value of $e = 3.41 \times 10^{-6}$.

In Hopkinson's experiments the compression ratio was higher than in those of Coker, being 6.37 as compared with 5.8, and T_1 would be approximately 2350°C . The mean piston temperature was 350°C .; and assuming $T = 300^\circ \text{C}$.

$$\phi^2 = \frac{1}{4} \left\{ \left(\frac{2650}{2} - 350 \right)^2 + \left(\frac{2050}{8} \right)^2 \right\},$$

$$= 369,000.$$

The mean value of h deduced from the temperature gradients across the piston is 1.43, making $e = 3.87 \times 10^{-6}$, a value 13 per cent. greater than that deduced from Coker's experiments. The difference is probably partly due to the greater density of the charge and partly a dimensional effect due to the relatively greater radiation per unit area at a given temperature from a large than from a small body of gas. Allowing for this, the two sets of results appear to be in close agreement.

Comparing these values with those deduced from Clerk's experiments on a gas-engine cylinder*, it appears that they are approximately 35 per cent. higher. This is to be accounted for by the fact that in Clerk's experiments the measurements were made over a number of successive expansion and compression strokes during which the turbulence would be appreciably less than on the stroke following admission of gas to the cylinder.

In the petrol-engine tests the compression ratio was varied from 4.6 to 5.3. The results showed that the piston-temperature gradient is only very slightly affected by the degree of compression, but that it is slightly less with the higher compression ratios. In these tests the maximum temperature of the working fluid can only be assumed; but it is certainly higher than in the gas-engine tests, and is probably in the neighbourhood of 2400°C ., except in the case of the author's tests on a cast-iron piston, where, on account of the richer mixture necessary for satisfactory operation, it would probably be about 2300°C . The minimum temperature of the working fluid has been taken at 250°C . In each of these cases the mean temperature of the piston between the points of measurement is known, and making the foregoing assumptions as to gas temperatures, the values of e become as shown in Table II.

* Section 9.

From these figures it appears that the values obtained for the various aluminium pistons are also in reasonable agreement, the difference between the mean value 8.9×10^{-6} deduced from Jardine and Jehle's tests at 800 r.p.m. and the author's mean value of 11.0×10^{-6} at 1800 r.p.m. being explained by the greater turbulence of the working fluid at the higher speeds of rotation. It will be noted that the latter value of e is three times as great as that obtained in the gas-engine tests, a difference which is also probably due mainly to the difference in turbulence.

The value of e deduced for the cast-iron piston in the author's experiments is, however, much lower than that found for the aluminium pistons. It is, in fact, only about one-half of the latter value. No complete explanation of this discrepancy can be put forward at the moment. It is probably partly due to the greater cooling effect of oil-splash on the under side of this hot piston, but mainly to carbon deposits on the piston crown.

7. Adopting the value 3.41×10^{-6} deduced from Coker's piston temperature-gradient measurements*, and using this in equation (6),

$$a = \frac{e\{(T_1 - \theta_0)^2 - (T_2 - \theta_0)^2\}}{2\sqrt{2\pi n\rho sk}},$$

the value of " a ," the semi-amplitude of the fluctuations of surface temperature, may be deduced, and this may be compared with experimental measurements of the fluctuation.

Adopting the same mean values as before, viz. $T_1 = 2120^\circ$, $T_2 = 270^\circ$, $\theta_0 = 230^\circ$, and taking for a cast-iron piston $\rho = 7.8$, $s = 0.11$, $k = 0.11$, n (at 200 r.p.m.) = $\frac{100}{60}$; this makes

$$a = \frac{3.41 \times 3.57}{2} = 60.1,$$

indicating a total fluctuation of 120.2°C .

The measured fluctuations of temperature at a depth of 0.02 in. (0.51 cm.) obtained from the tables given in the paper have a mean value of 29°C . It may readily be shown that the fluctuation of temperature at any depth x is proportional to

$$e^{-\sqrt{\frac{\pi n \rho s}{k}} x} \quad \dagger,$$

so that for cast iron at 100 cycles per minute the corresponding surface fluctuation would be 40°C ., which is much higher than the value (120.2°C .) calculated. It was however

* Proc. Inst. C. E. vol. xcvi. pt. ii. (1913-14).

† Here e is the base of the Napierian logarithms.

pointed out in the discussion on the paper that there is reason for thinking that the measured values may have been greater than the true cyclical fluctuation, and in earlier tests on the same engine a measured fluctuation of temperature of $7^{\circ}\cdot 2$ C. was obtained at 240 r.p.m. at a depth of $\cdot 015$ in. in the metal of the combustion space, corresponding to a surface fluctuation of $9^{\circ}\cdot 3$ C., which would be equivalent to a fluctuation of $10^{\circ}\cdot 2$ C. at 200 r.p.m.

8. Measurements of the fluctuation of temperature at the centre of the head of the inlet valve and of the exhaust valve of the same engine at a depth of $\cdot 02$ in. at 200 r.p.m. gave mean values of 15° C. and 12° C. respectively, corresponding to surface fluctuations of $20^{\circ}\cdot 7$ and $16^{\circ}\cdot 5$. The mean temperature of the inlet valve was 250° C. and of the exhaust valve 370° C. Taking $T_1 = 2120^{\circ}$ C., T_2 for the exhaust valve $= 320^{\circ}$ C., and T_2 for the inlet valve $= 100^{\circ}$ C. owing to the influx of cold mixture during the suction stroke, this makes $e = 5\cdot 90 \times 10^{-6}$ for the inlet valve and $e = 5\cdot 43 \times 10^{-6}$ for the exhaust valve. These values are 70 per cent. greater than those deduced from the piston—a difference which is to be expected owing to the velocity of flow over these valve surfaces during the inlet and exhaust strokes.

9. Clerk's experiments on the rate of cooling of the gases in the cylinder of a gas engine during repeated expansions and compressions after explosion * are valuable as indicating the effect of temperature on the interchanges of heat under these conditions. The experiments on this engine, which has a bore of 14 in. and a stroke of 22 in., were carried out at 160 r.p.m. The compression ratio was 6:1, so that the density during the period of heat transmission ranged from 1 to 6 approximately. Taking the mean temperature throughout a complete stroke, Clerk gives the following values (line 2) for the heat-loss per second per sq. ft., based on the area exposed when the piston is full out †:—

Mean temperature, °C.	1400°	1300°	1150°
Heat-loss in cub. foot, degrees per sec.	400	340	260
$h + (T_0 - \theta_0)^2$	$1\cdot 63 \times 10^{-6}$	$1\cdot 66 \times 10^{-6}$	$1\cdot 68 \times 10^{-6}$
$e \times 10^6$	2\cdot 28	2\cdot 30	2\cdot 31

In these experiments the mean temperature of the cooling surfaces was 190° C. Converting the heat-loss into C.G.S. units, and dividing by $(T_0 - \theta_0)^2$, where T_0 is the mean gas temperature, gives the values shown in line 3 of the above table. From the data given in the original paper it is

* Proc. Roy. Soc. A, lxxvii, p. 499 (1906).

† Clerk, 'The Gas, Petrol, and Oil Engine,' vol. i. p. 230 (1909).

possible to determine the approximate values of T_1 and T_2 in each case, and so to get the mean square of the temperature difference as defined in expression (7). Making this correction, and assuming that the mean exposed area during the stroke is that exposed at half-stroke, the new values for e ($=h/\phi^2$) become as shown in line 4. These values are of the same order, but about 35 per cent. less than the values obtained in the experiments of Coker and Hopkinson; and when due weight is given to the difference in the conditions as regards turbulence in the two sets of experiments, the agreement would appear to be satisfactory.

10. The foregoing results indicate that the value of e to be used in calculations of the probable heat-flow at any point of a given piston by the use of formula (1), (2), or (3), depends largely on the turbulence of the working fluid. At the compression ratios usual in practice, and under normal working conditions, it ranges from about 3.6×10^{-6} in a slow-speed gas-engine at 200 r.p.m. to 11.0×10^{-6} in a high-speed petrol-engine at 1800 r.p.m.

Adopting these values, it is of interest to calculate the probable fluctuations of surface temperature.

In a petrol-engine making 1800 r.p.m. having an aluminium piston, $n=15$, $\rho=2.9$, $s=0.21$, $k=0.38$, and the value of $\pi n p s k$ in C.G.S. units is 11.0, a value which is large compared with e .

Under these conditions

$$a = \frac{e\{(T_1 - \theta_0)^2 - (T_2 - \theta_0)^2\}}{2\sqrt{2\pi n p s k}},$$

and assuming $T_1=2400^\circ\text{C.}$, $T_2=250^\circ\text{C.}$, $\theta_0=250^\circ\text{C.}$, this makes

$$a = \frac{11.0 \times 4.63}{9.4} = 5.5^\circ\text{C.},$$

or a total surface fluctuation of 11.0°C.

For a cast-iron piston, $\rho=7.8$, $s=0.11$, $k=0.11$, and adopting the same values for e , T_1 , and T_2 , but assuming $\theta_0=400^\circ\text{C.}$,

$$a = \frac{11.0 \times 4.65}{6.23} = 8.2^\circ\text{C.},$$

or a total fluctuation of 16.4°C.

From these figures it is apparent that, even making allowance for a considerable error in the value of e , the fluctuation of surface temperature at such speeds is negligible.

11. *Experimental Verification.*—The difficulty of experimentally measuring the surface fluctuation in an engine at

very high speeds is almost insuperable, and to avoid this the author carried out a series of experiments * which, though not directly representing the conditions obtaining in the metal of the piston of an engine, approximate to these.

The experiments were carried out on a series of bars of aluminium-copper-zinc alloy, having a composition of Al, 92 per cent.; Cu, 7 per cent.; Zn, 1 per cent. The eutectic melting-point of this alloy was carefully measured, and found to be 540°C . The bars are $\frac{3}{8}$ in. diameter and 6 in. long. One end of each bar was turned down to $\frac{1}{8}$ in. diameter for a length of $\frac{1}{8}$ in., and an asbestos washer 3 in. diameter was fitted against the shoulder thus formed. A Pt Ir thermocouple was plugged into the bar at a point $\frac{3}{16}$ in. from this end. The bar was clamped horizontally.

A sheet-steel sliding shutter having a central $\frac{1}{2}$ in. square hole was operated by an electric motor, and made 450 reciprocations per minute immediately in front of the turned end of the bar. When the shutter is in the middle of its travel, the blast from a blowpipe (flame temperature approximately 1650°) impinges directly through the hole in the shutter on to the turned end of the bar. Owing to the motion of the shutter, the end of the bar is thus subjected to an intense heat 900 times per minute. The total period during which the flame is in contact with the bar is approximately one-fourth of each cycle. The conditions thus approximate fairly well to those obtaining in the metal of an aero-engine making 1800 revs. per minute. Each experiment lasted for 50 minutes, after which the bar was cut in two along the axis and was polished, etched, and examined microscopically.

In carrying out a test the blowpipe was turned full on. The temperature of the thermocouple was then observed until it became steady. This temperature was generally about 350°C . A bunsen burner was then placed under the further end of the bar, and was adjusted until the thermocouple gave steady readings at the desired temperature.

The following table shows the results of the tests :—

Bar No.	Temperature at thermocouple.	Results of micro. examination.
1.	526°C	No change in structure.
2.	536°C	" "
3.	550°C	Eutectic segregated over whole mass of bar up to 1 inch from heated face. No apparent difference between heated face and interior of bar near face.

* Advisory Committee for Aeronautics. L.A.S.C. Reports, No. 13, p. 18 (May 1918).

The fact that no segregation of the eutectic even at the exposed and heated face was observed when the mean temperature at a point $\frac{1}{16}$ in. deep was as high as 536°C . indicates that the fluctuation of surface temperature must have been appreciably less than 4°C . Calculations based on the known gas temperatures, using formula (6), show that this should be approximately $1^{\circ}\cdot 5^{\circ}\text{C}$.

12. *Conclusions.*—The investigations would point to the following conclusions:—

(1) Assuming that the heat transference from a hot gas to a metal surface per second per unit area equals $e\phi^2$, where ϕ is the difference of temperature in degrees centigrade, the mean rate of heat transmission throughout the cycle under the conditions obtaining under normal conditions of operation in engines having compact cylindrical combustion chambers with compression ratios between 4·5 and 6·5 is very approximately equal to

$$e \times 25 \left[\left\{ \frac{T_1 - T_2}{2} - \theta_0 \right\}^2 + \frac{(T_1 - T_2)^2}{8} \right],$$

where T_1 and T_2 are the maximum and minimum gas temperatures and θ_0 is the mean temperature of the metal surface.

For the piston and combustion head surfaces, e has a value which varies from about $3\cdot 6 \times 10^{-6}$ in gas-engines of 6 to 12 in. diameter at speeds in the neighbourhood of 200 r.p.m. to $11\cdot 0 \times 10^6$ in high-speed petrol-engines at about 2000 r.p.m. These values are in C.G.S. units. The corresponding values expressed in C.H.U. per sq. ft. per minute are $4\cdot 4 \times 10^{-4}$ and $13\cdot 5 \times 10^{-4}$.

(2) The semi-amplitude of the cyclical fluctuation of surface temperature on the same assumptions is given by

$$a = \frac{e[(T_1 - \theta_0)^2 - (T_2 - \theta_0)^2]}{2\sqrt{2\pi n p s k}}.$$

Owing to the velocity of flow over their surfaces, the values of e to be adopted in calculations of the fluctuation of temperature in exhaust or inlet valves are approximately 70 per cent. greater than those given above.

(3) In a high-speed petrol-engine at 2000 r.p.m. the fluctuation of temperature in the surface of the piston, if of aluminium, is of the order $\pm 5^{\circ}\text{C}$.

(4) In conclusion the author would emphasize the fact that owing to the comparatively limited amount of available data, and the assumptions which have had to be made regarding the temperatures of the working fluid, the foregoing values for e can only be considered as approximate. In spite of the difference in the methods by which they have been deduced, they do however show a satisfactorily close agreement; and it is hoped that the accumulation of data on these or other lines will enable more close accurate values to be deduced in due course.

APPENDIX.

Let T_1 be the maximum temperature of the gas,

T_2 „ minimum „ „

T_0 „ mean „ „

θ_0 be the temperature of the surface (supposed constant),

$h = e(T - \theta_0)^2 =$ heat transmitted from gas to surface
per second per unit area,

$n =$ no. of cycles per second.

Then heat transmitted per sq. cm. per cycle

$$\begin{aligned} &= \frac{2e}{2\pi n} \int_{\pi/2}^{3\pi/2} \left\{ T_0 - \theta_0 + \left(\frac{T_1 - T_2}{2} \right) \sin \theta \right\}^2 d\theta, \\ &= \frac{e}{n} \left\{ (T_0 - \theta_0)^2 + \frac{(T_1 - T_2)^2}{8} \right\}, \\ &= \frac{e}{n} \left\{ \left(\frac{T_1 + T_2}{2} - \theta_0 \right)^2 + \frac{(T_1 - T_2)^2}{8} \right\}. \end{aligned}$$

Mean heat inflow per sec. per sq. cm.

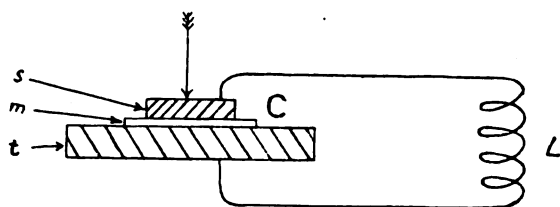
$$= e \left\{ \left(\frac{T_1 + T_2}{2} - \theta_0 \right)^2 + \frac{(T_1 - T_2)^2}{8} \right\}.$$

LXXXVIII. *A Valve Method of Detecting Minute Slipping in Metals.* By ORCIL HANDFORD, M.Met.

[Plate VI.]

1. IT was required in the course of an investigation on the fatigue of metals to determine the stress which produced the first minute slips in a specimen under tension, that is, the point at which the elastic limit of the metal was locally exceeded in one or more crystal grains. For this purpose a polished surface was examined while the specimen was under stress, in order to observe the first appearance of the well-known slip-bands. This method proved to be insufficiently sensitive, no slip-bands being visible under a low or high magnification until the actual amount of slip was considerable. As a rule the faint ruffling of the surface could be perceived by the unaided eye, under proper condition of illumination, as soon as by means of the microscope, and this in spite of very numerous experiments in the direction of more suitable methods of illumination. A method depending on the alteration of capacity of a condenser, and making use of thermionic valves, was therefore tried. This method was suggested by the description of Professor Whiddington's valve Ultra-micrometer, given to the Wireless Society of London, December 21st, 1920. His arrangement was modified in accordance with the following description, to suit it to the problem in hand and the laboratory conditions prevailing.

Fig. 1.

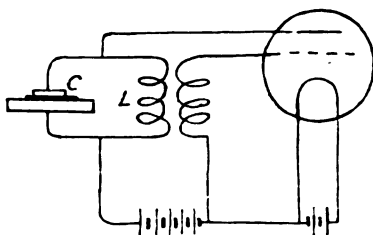


2. A piece of metal, *s*, having one face accurately levelled and polished, is held by spring pressure against the levelled and polished surface of the test-piece, *t*, but separated from it by a very thin plate of mica, *m*. This forms a condenser, *C*, across which is joined an inductance, *L*, forming an oscillatory circuit (fig. 1). This circuit is connected to a

* Communicated by Professor C. H. Desch, F.R.S.

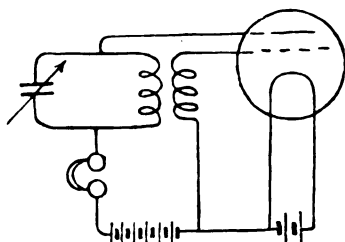
three-electrode thermionic valve so as to oscillate at its natural frequency (fig. 2).

Fig. 2.



A second similar circuit is formed having a small variable condenser instead of the one formed on the surface of the test-piece, and is adjusted so as to oscillate at a slightly lower frequency (fig. 3). Included in this second valve circuit is a pair of telephones.

Fig. 3.



Let the two frequencies of oscillation be f_2 and f_1 respectively. The two circuits are coupled together so that the oscillations of the first circuit are impressed on the second. There will then be beats of amplitude of oscillation in the second circuit, occurring at the rate of $f_2 - f_1$ per second. These beats on rectification will give a musical note of frequency $f_2 - f_1$ in the telephones.

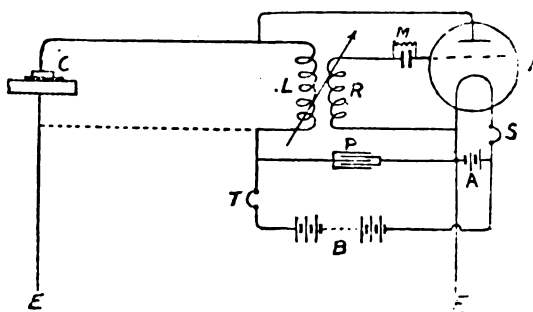
If the surface of the test-piece becomes distorted in any way, the small auxiliary plate will be pushed away and the average distance between the two surfaces increased. The resultant decrease in capacity of the condenser which they form will raise the frequency of the first oscillatory circuit to, say, f_3 .

The beat-note appreciated in the telephones will now be $f_3 - f_1$, a higher note. Thus, under these conditions, a rise in note in the telephones indicates distortion of the test-piece surface.

The method is sensitive because the frequency of the first circuit varies inversely with the capacity of its condenser, while the indication given in the telephones is its arithmetical change. Hence, by making the oscillation frequency very high and the datum beat-note in the telephones very low, large changes of pitch are obtained for very small variations in the capacity of the condenser. After experiment an oscillation frequency of 10 million was decided on, as being the highest that could be generated and handled easily.

3. The actual apparatus used consisted of two units, the "Transmitter," whose condenser is made up of the test-piece and auxiliary plate, and the "Receiver" containing the telephones. The complete circuit diagram of the Transmitter is shown in fig. 4.

Fig. 4.



Circuit diagram of "Transmitter."

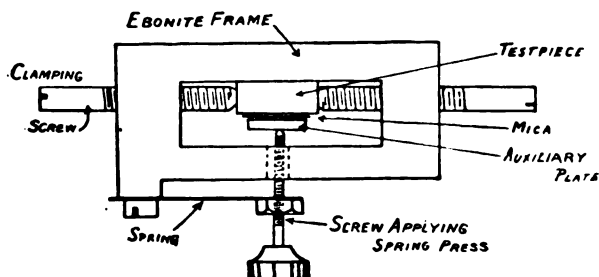
The inductance, L , of the oscillatory circuit consists of a spiral winding of $9\frac{1}{2}$ turns 28 gauge S.S.C. copper wire, $1\frac{1}{2}$ inches internal diameter. Its inductance is 2.30 microhenries. The reaction coil, R , consists of a similar winding of $7\frac{1}{2}$ turns, approximately 1.5 microhenries in inductance. The auxiliary plate forming the condenser, C , with the test-piece is held in an ebonite frame (fig. 5) which clamps lightly on to the test-piece by ebonite screws. The mica used is .0002 to .0005 in. thick, and the plate .4 in. square.

The valve, V , is a Mullard "Ora," which is found to oscillate easily under adverse conditions. The battery, A , is a four-volt accumulator of 100 ampere hours capacity. This large capacity ensures constancy of filament current, which is a necessity, as the frequency of oscillation is not

quite independent of filament temperature. A switch, S, controls this battery.

A plate voltage of 90 is necessary to enable the valve to oscillate under the adverse conditions obtaining. This is supplied by the dry cell battery, B. A bye-pass condenser, P, of .002 microfarad is connected as shown to enable the high frequency currents to avoid the inductance of the battery B and its leads, and, when used, telephones at T. These terminals are used to insert a pair of telephones for testing purposes only. They are normally short-circuited. The filament battery is connected to the frame of the testing machine as shown at E. The test-piece is, of course, similarly connected by the gluts (fig. 5). Thus the oscillatory circuit L, C, has its lower junction completed through the

Fig. 5.



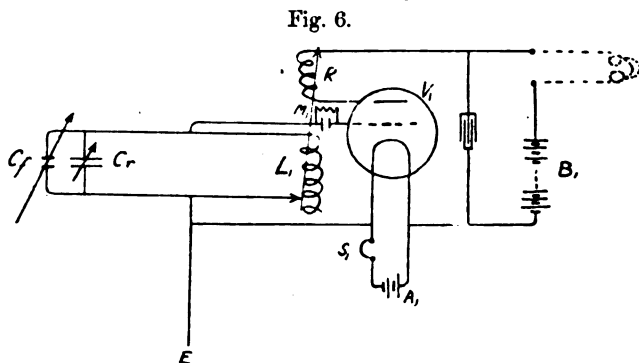
Frame holding auxiliary plate.

condenser P, whose impedance at 10 million frequency is very small. This is preferable to earthing the lower end of L to the testing machine, as the accumulator A would then be at 90 volts negative potential to earth with consequent current leakage from the battery B and possible damage to the cases of the accumulator A. A resistance, M, of several megohms is connected in the grid circuit so as to cause the electronic discharge on to the grid to maintain its mean potential at -6 volts. This compensates for the fact that 90 volts is used on the plate whereas the valve is designed for 30 volts. To prevent high frequency losses in M it is shunted by a condenser of .0005 microfarad capacity. The small size of the reaction coil is necessitated by the fact that the frequency at which the circuit L, C will oscillate is not independent of the natural frequency of the reaction coil given by its inductance, its self-capacity, and the plate-filament capacity of the valve, which acts across it, but is nearly so if this natural frequency is much greater than that of the circuit L, C. The coil used as reaction coil has a natural frequency

3 M 2

of about 50 million when connected to the valve. The coupling between the main inductance and reaction coil is made variable so as to control the amplitude and stability of the oscillations.

The Receiver circuit is shown in fig. 6.



Circuit diagram of "Receiver."

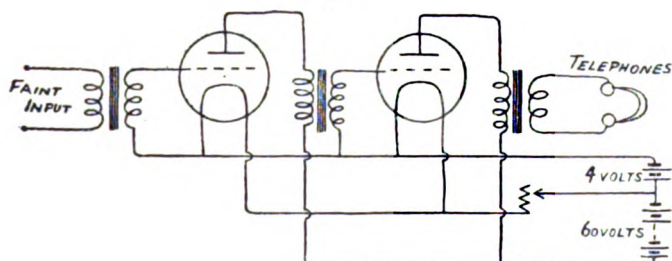
The inductance L_1 consists of a spiral winding of $11\frac{1}{2}$ turns, tapped at $7\frac{1}{2}$, $9\frac{1}{2}$, and $11\frac{1}{2}$ turns so as to give a wide range of frequency and a choice of L/C ratios, which latter is desirable to secure a suitable degree of stability of the oscillations produced. The approximate inductances are 1.4, 2.3, and 3.4 microhenries. The reaction coil R_1 is a spiral winding of 11 turns and inductance approximately 3.3 microhenries. The condenser forming the remainder of the oscillatory circuit is divided into two, C_r , of approximate range .00001 to .0002 mfd., and C_f , approximately .00001 to .00002 mfd. By a system of gearing, this last condenser is made capable of very critical control, and is used for fine adjustment of the frequency.

A French "R" type valve, V_1 , is used in this circuit owing to its all round efficiency. A four-volt accumulator of 100 ampere hours capacity, A_1 , and 60 volt dry battery, B_1 , supply filament current and plate voltage respectively. Rectification of the beats of amplitude of oscillation is provided for by the leak and resistance, M_1 , of $1\frac{1}{2}$ megohms and .0001 mfd. capacity. The unilateral conductivity of the grid-filament space causes alternating voltages applied to the grid from the main oscillatory circuit to give negative charges to the grid varying with their amplitude. This causes non-symmetrical reproduction in the plate circuit which can be resolved into symmetrical and unidirectional components. The unidirectional component affects the

telephones. The mean potential of the grid is maintained at a suitable value by the $1\frac{1}{2}$ megohm leak. The coupling between the main inductance, L_1 , and reaction coil, R_1 , is again made variable so as to afford control of the stability of oscillation.

When the receiver and transmitter are coupled together and adjusted so that their difference of frequency is very small they tend to pull one another into step, and the beat-note disappears. This tendency is reduced by making the coupling between the two units very small, and arranging the stability of oscillation of the two circuits to be approximately the same. It proves necessary to have the receiver and transmitter six feet apart, and to take great care that the loop formed by the earthing and condenser leads on the transmitter is at right angles to the direction of the receiver. This results in a beat-note so faint as to be inaudible above ordinary laboratory noises, and two further valves are therefore used as low frequency amplifiers to give a note of convenient loudness. The diagram of this part of the apparatus is shown in fig. 7.

Fig. 7.

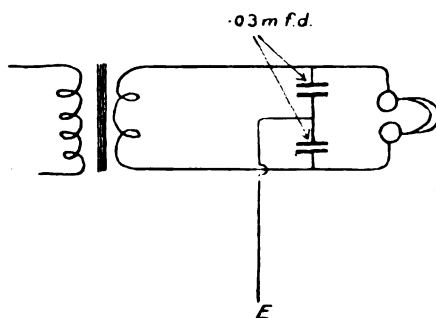


Low frequency amplifier.

Owing to the sensitivity of the apparatus to capacity changes, it is strongly affected by the movement of persons in its neighbourhood. The operator stands on the opposite side of the pillar of the testing machine to that on which the transmitter is placed, the pillar acting as a screen. The operator's body is earthed by the insertion, in the stocking, of copper gauze connected to earth. Since, however, the inductance from hand to foot is not negligible at 10,000,000 frequency, this does not entirely stop changes of beat-note from occurring when the machine is handled. A thick leather glove is therefore worn during tests. It is found necessary to join all metallic masses in the laboratory together and connect them to the filament circuit of the

receiver and to the testing machine in order to avoid changes of beat-note when the operator moves in their neighbourhood. Though removed from the oscillatory circuit by three transformers and two valves, the telephones have sufficient capacity coupling to it to cause changes of beat-note when their pressure on the operator's head varies. They are therefore earthed in the manner shown in fig. 8.

Fig. 8.

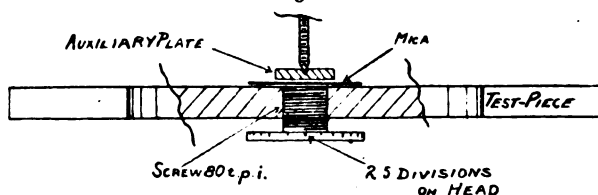


System of earthing telephones.

Photographs of the apparatus are appended (Pl. VI.).

4. The frequency of oscillation is checked before each test by means of a low-range heterodyne wavemeter designed for wireless telegraphy. Readings are taken of the settings of this instrument at which its harmonics are heard in the receiver. These values divided by consecutive numbers, found by trial, give a constant—the wave-length of the set, from which its frequency can be calculated. The wave-length can easily be kept between 35 and 28 metres, corresponding to frequencies of 9.8×10^6 and 12.5×10^6 .

Fig. 9.



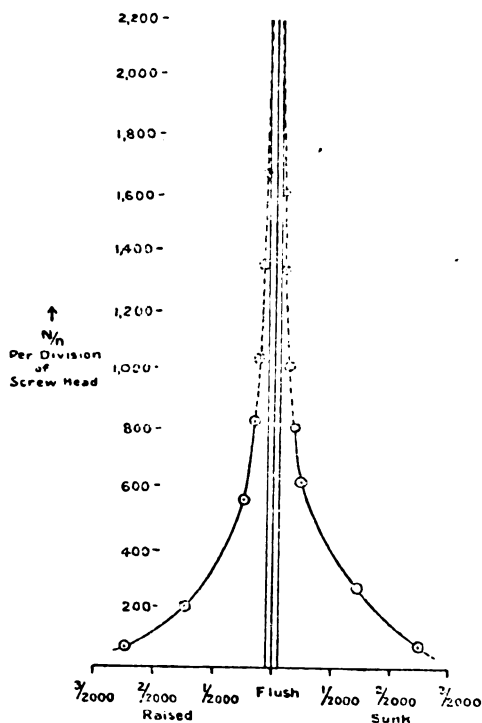
5. An approximate estimate of the sensitivity of the instrument has been made in the manner shown in fig. 9.

Artificial distortion of a dummy test-piece is produced by means of a screw of 80 threads per inch let into it. The

face of the screw is ground and polished level with the face of the test-piece, and the head divided into 25 parts, so that if the head is rotated, each division represents a rising or sinking of the face of the screw by $1/2000$ th of an inch.

As the face of the screw is arranged to be half the area of the auxiliary plate this corresponds to a slip in which half the test-piece remains in contact with the mica and half sinks to a depth of $1/2000$ inch, or one in which half

Fig. 10.



the surface of the test-piece rises to a height of $1/2000$ inch. A divided head is fitted to the fine adjustment of the receiver condenser, and readings taken of the rotation (N) required to produce the same change of beat-note as various movements of the head of the screw in the dummy test-piece, and that (n) required to produce the smallest change in the datum beat-note accepted as a slip indication during tests. The results are shown in full line in fig. 10.

The change of capacity of the condenser for a given minute movement of the plates will, as is indeed apparent from the plotted results, be very much greater when they are almost touching the mica than when they are spaced apart from it by only a very small distance. As $1/4000$ and $1/2000$ inch are very large compared with the slip during a test, it is necessary to make use of extrapolation. The curves will be approximately of the same shape as those showing the variation of capacity of a condenser with the distance between its plates, and, using this as a guide, the curves are produced (as shown dotted) till near the line indicating the flush position of the screw face. The maximum rate of change of capacity attainable with the instrument occurs when the metal surfaces are touching the mica. The movement of the screw face has been in air. Hence, on the horizontal scale, the $3/10,000$ of mica used will be represented by $1/20,000$ inch of air, since the specific inductive capacity of mica is about six. Hence, lines drawn parallel to the "flush" line and separated from it by $1/20,000$ inch will cut the extrapolated curves at the value of N/n which would be attained if it were possible to move the screw face through $1/2000$ inch while keeping its average distance from the mica zero.

This intersection occurs at $N/n=2000$.

Thus the sensitivity is

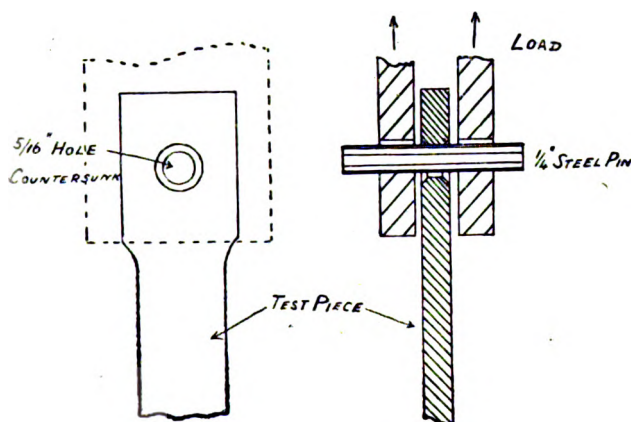
$$\begin{aligned} & \frac{n}{N} \times 2000 \text{ in.} \\ &= 2000 \times \frac{1}{2000} \text{ in.} \\ &= 25 \times 10^{-6} \text{ in.} \\ &= 6.5 \times 10^{-6} \text{ mm.} \\ &= 65 \text{ \AA units.} \end{aligned}$$

Owing to the extrapolation and approximations involved, this figure can only be regarded as a rough indication of the order of magnitude of the smallest slips observed.

6. Two general observations of interest were made with the instrument. Knife-edge friction in the beam-testing machine employed tended to swing the top glut outwards when the beam fell, and inwards when it rose. This caused a slight general bending of the test-piece, which gave a rise of note in the telephones. This rise in note was considerably diminished by dispensing with gluts and loading the test-piece axially in the manner shown in fig. 11.

In an attempt to eliminate it entirely, the auxiliary metal surface used to oppose the test-piece surface was made of tinfoil backed by a block of soft rubber forcibly pressed by a screw on to the face of the test-piece. A rise in note on putting on load was still observed however, and the rise in note was now the same whether the test-piece were loaded axially or not, and even when wedge-shaped packing was put in the gluts to give big bending stresses.

Fig. 11.



Method of applying axial loads.

Provided that the load was not such as to cause the metal to behave non-elastically, the note returned to datum when the load was taken off. It seemed clear that the rubber-backed condenser plate had compensated for general bending of the test-piece, and that the effect was due to elastic inequalities of the surface of the test-piece, caused by the stress applied.

In carrying out ordinary tests, when a load was reached which gave a yield, it was observed that the note in the telephones did not assume its highest pitch at once, but during a period of from half a second to five seconds. The rate of rise was great at first and gradually decreased till imperceptible. That this lag was not due to the testing machine or valve instrument was proved by the rapidity with which elastic strains were indicated. It therefore became apparent that this was an early stage of the time lag which

takes place in a yield, the later stages of which have been described previously ("Surface Tension Effects in the Intercrystalline Cement in Metals and the Elastic Limit," F. C. Thompson, Jour. I. S. I., 1916, No. 1, pp. 186-7).

7. Time was not available for many tests, and in view of the fact that further work is required before they can be discussed from a metallurgical point of view, only a few experimental results are given showing some of the possibilities of the instrument. A 70/30 Brass, in the annealed condition, of maximum stress 10 tons per sq. in. and safe fatigue range (Haigh machine) 10 tons per sq. in., had an elastic limit as determined visually of 2.7 tons per sq. in. The valve slip indicator showed slip at 2.4 tons per sq. in. Annealed 80/20 Cupro-nickel gave very similar results.

A 0.25 per cent. Carbon Open-hearth Steel, normalized, had a maximum stress of 35 tons per sq. in., a safe fatigue range (Haigh machine) of 24 tons, and elastic limit (Metzger Extensometer) of 16 tons per sq. in. The valve slip indicator showed a slip at 14.2 tons per sq. in.

In all the above cases, the valve slip indications were very sharp in character and great in magnitude, and increased rapidly on further loading, up to fracture.

Annealed Copper used had a maximum stress of 15 tons per sq. in., a safe fatigue range (Haigh machine) of $11\frac{1}{2}$ tons per sq. in., and an elastic limit (visually determined), of about 4 tons. With the valve slip indicator it showed faint slip at very low loads of .1 to .4 ton per sq. in. Faint slip continued until a load between 3 and 4 tons per sq. in. was reached, when comparatively sharp and heavy slip, increasing on further loading up to fracture, was observed. Between the point at .1 to .4 ton and that at 3 to 4 tons, the faint slip appeared to be discontinuous, increasing abruptly at two points near 1.2 tons and 2.0 tons per sq. in., but these points were not very sharply marked and their existence is not considered as definitely proved.

Annealed Nickel gave similar results. Very faint slip began at .6 ton per sq. in., and a definite yield occurred at about 6 tons per sq. in. There appeared to be a discontinuity in the slip prior to 6 tons per sq. in., at about 3 tons per sq. in. The maximum stress of this material was 31.2 tons per sq. in., its safe fatigue range (Haigh machine) 37 tons, and elastic limit (visually determined) 25 tons per sq. in.

FIG. 1.

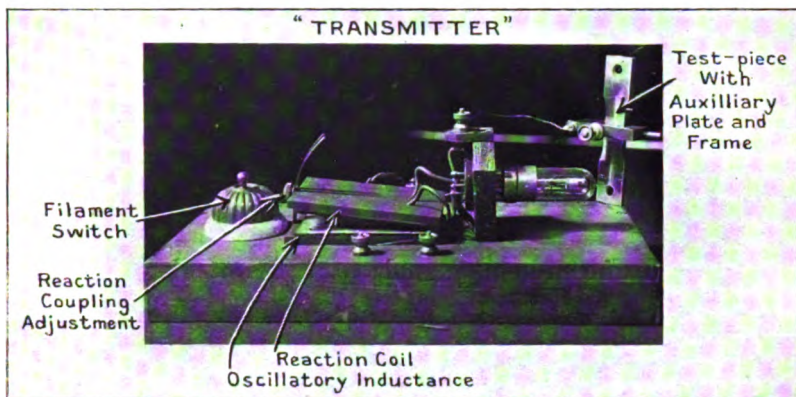
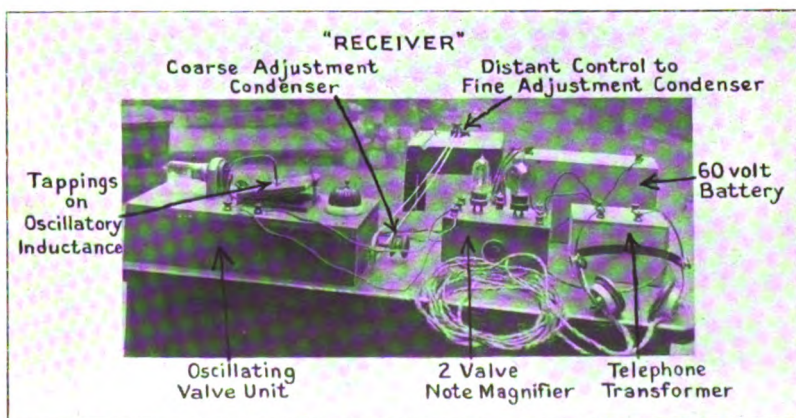


FIG. 2.



8. The work described was done in the Faculty of Metallurgy, University of Sheffield, in 1922, with the aid of a grant from the Department of Scientific and Industrial Research, and under the supervision of Professor Desch.

The author feels very deeply indebted to Professor Desch, whose keen interest and generous aid has contributed very largely to whatever success has been attained.

He desires also to thank the Staffs of the Faculties of Engineering and Metallurgy, who have assisted in many ways, especially by the loan of apparatus, and in the preparation of test-pieces.

LXXXIX. *Determination of the Curvature Invariant of Space-Time.* By L. SILBERSTEIN, Ph.D.*

THE empty space-time which was originally proposed by de Sitter as a solution of Einstein's amplified field-equations, and which possesses the more important property of being perfectly isotropic with respect to Riemannian curvature, is characterized by the line-element

$$ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - dr^2 - R^2 \sin^2 \sigma (d\phi^2 + \sin^2 \phi d\theta^2), \quad (1)$$

where $\sigma = r/R$. The space-part of this quadratic form is the line-element of an elliptic space which will be assumed to be of the *polar* or properly elliptic kind, so as to be covered by the interval $\sigma = 0$ to $\sigma = \frac{1}{2}\pi$. The constant R is the curvature radius of this space (as a particular section of the fourfold) and, what is more important, an *invariant of the space-time*; if G be the invariant of the curvature tensor G_{ik} , the radius R as appearing in (1) is given by $G = 12/R^2$. In fine, R has an intrinsic meaning and, if it is at all finite, it is manifestly of prime interest to determine it from a number of independent sets of observational data and to see whether the R -values thus obtained are more or less consistent with each other.

It is the purpose of this paper to show that such is very likely the case. Very likely, that is, inasmuch as the now available data yield, with the aid of a Doppler effect formula to be derived presently, nine R -values, seven from globular clusters and two from the Magellanic Clouds, which seem to be fairly consistent with each other and do not clash with the generally accepted views of the known universe.

* Communicated by the Author.

De Sitter's own attempt to that effect is well known from his paper (M. N., R.A.S., Nov. 1917) and from text-books on Relativity. It was based on the artificial assumption of a star coerced to remain at a fixed distance r from the observer, and led to a spectrum-shift or, as we will henceforth say, a *Doppler effect**, $D = \delta\lambda/\lambda$, which by the first term of (1) should be

$$D = \frac{1}{\cos \sigma} - 1 \doteq \frac{1}{2}\sigma^2.$$

The characteristic feature of this formula was that it predicted always a positive D or a *red-shift*. Its application to the B -stars, which show such systematic shifts of about 4.5 km./sec., gave $R = 6.7 \cdot 10^9$ astr. units, one third of the effect being attributed by de Sitter to the gravitation fields of the stars themselves. Apart from being too small, this value stood alone, not being supported by other values derivable by means of the same formula from other celestial objects. The Lesser Cloud, as quoted by de Sitter *loc. cit.*, rather contradicted the B -stars' value, offering one of the order 10^{11} at the least. The important point, however, is that de Sitter's formula cannot be applied to actual stars, if these, as well as the observing station, are to behave as free particles, describing world-geodesics. For such particles cannot, in the space-time (1), be at rest relatively to each other even a single instant, unless they coalesce or one is at the polar of the other. Thus, to be of any use at all, the Doppler effect formula ought to be constructed for a star and an observer in free inertial motion, each describing some geodesic $\delta \int ds = 0$ of de Sitter's space-time (1) or, in view of the practically evanescent transversal effect, a geodesic of its two-dimensional section

$$ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - R^2 d\sigma^2, \quad . \quad . \quad . \quad (1a)$$

covering the sub-case of all radial motions.

This broader problem was recently taken up by Weyl †, whose merit it is to have formulated a general principle for computing intrinsically any such Doppler effect. The principle, which naturally suggested itself, is

$$D = \frac{ds}{ds'} - 1, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Whether it be associated with a relative motion of source and observer or not.

† *Raum-Zeit-Materie*, 5th ed., 1923, Anhang iii., and *Phys. Zeitschr.* 1923, p. 230.

where ds is the element of the observer's world-line cut out by the light-cones (in the present case the minimal lines of the twofold r, t) having their apices at the points s' and $s' + ds'$ of the star's world-line. The meaning of the formula is obvious, ds/ds' being the ratio of the proper times of the receiver and the sender. Its validity for actual spectrum comparisons is, of course, conditioned by the hypothetical permanence of atoms as "natural clocks" in Einstein's sense of the word, a much debated hypothesis which will here be accepted.

Unfortunately, applying this general principle (2) to the problem in hand, Dr. Weyl introduced the perfectly gratuitous assumption, more or less disguised as a necessary feature of de Sitter's world, according to which the world-lines of all the stars belong to a "pencil of geodesics diverging towards the future"—which, in plain English, amounts to assuming that some time ago the stars were all assembled and rather crowded around some place and had, there and then, evanescent relative velocities, to grow later on into huge and (apart from gravitation) ever increasing positive radial motions. With this arbitrary hypothesis, and through a number of rather obscure technicalities*, Weyl's formula became

$$D = \tan \sigma,$$

with a unique positive sign, yielding always a red-shift or what the astronomers call a *positive* "radial velocity." Dr. Weyl himself insists on this feature as a result of his sublime guess about the remote past of all the stars. An echo of this "universal scattering tendency" of matter resounded in Eddington's 'Mathematical Theory of Relativity,' where some curiously fallacious remarks are made in connexion with this subject. But, no matter how unlikely and how arbitrary, Weyl's hypothesis is entirely undesirable, as it is flatly contradicted by the famous nebula in Andromeda, showing an effect of $c/D = -300$ or -316 km./sec., by one or two more spirals, though these do show a preponderance of positive or red-shifts, and by a host of equally interesting and probably as distant celestial objects, the globular clusters. Among the latter, negative radial velocities are by no means an exception. Rather the contrary.

Under these circumstances it has seemed worth while to

* Some of these, which the reader may try to extricate, *loc. cit.*, are responsible for 'tan' instead of $\sin \sigma$; but this is of little importance, as in all hitherto accessible cases both reduce to σ .

investigate the problem from the outset, basing its solution on de Sitter's theory unsupplemented by any such arbitrary assumptions by which it was unnecessarily limited or actually mutilated.

The equation of a geodesic of the twofold (1 a), representing the most general radial motion of a free particle, is easily found to be

$$\frac{R}{c} \frac{d\sigma}{dt} = \pm \cos \sigma \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2}} \equiv \pm \frac{v}{c}, \quad . . . \quad (3)$$

where the signs correspond to a receding and an approaching particle respectively, and γ is an integration constant, $\cos \sigma \cdot c dt/ds = \gamma$, which, with β written for v_0/c , has the meaning

$$\gamma = (1 - \beta^2)^{-1/2},$$

and is, therefore, essentially greater than, though but slightly differing from, unity. Thus, as mentioned before, v can be zero only for $\sigma = 0$ or $\sigma = \frac{1}{2}\pi$. At any intermediate distance the two particles, say at $r = R\sigma$ and at $r = 0^*$, have necessarily some non-vanishing, either receding or approaching, radial motion relatively to each other. The corresponding acceleration is, still rigorously, determined by

$$\frac{R^2}{c^2} \frac{d^2\sigma}{dt^2} = \frac{1}{2} \sin 2\sigma \left(\frac{2 \cos^2 \sigma}{\gamma^2} - 1 \right), \quad . . . \quad (4)$$

with the same sign for both receding and approaching motion. Thus, up to a distance $\sigma_1 = \arccos(\gamma/\sqrt{2})$, which practically will be but little below 45° , the two particles do in fact behave as if they repelled each other. This, however, does not prevent the motion being, at any distance, either an approaching or a receding one. Moreover, beyond σ_1 or, practically, beyond the midpoint between the observer and his polar the acceleration itself of, say, a star will be negative, as if it were attracted by the observer †. At any rate, there is not the slightest reason for excluding negative velocities. It is true that a star which left the observer with an almost evanescent radial velocity ($v_0 \div 0$, $\gamma \div 1$) would continue to recede from him with a velocity growing up to $v = \frac{c}{2}$ at the midpoint, then only to fall off towards the polar. But, in quite the same way, one that left the polar with an almost evanescent velocity would approach us with a velocity

* Notice that $r = \text{const.} = 0$ is one of the world-geodesics (3).

† Notice in passing that the volume of the sphere $\sigma = \frac{\pi}{4}$ bears to that of the remaining elliptic space the ratio $(\pi - 2) : (\pi + 2)$. Thus, if the stars are more or less uniformly distributed, there are to every 'repelled' star about five which behave as if 'attracted' by the observer.

increasing up to the midpoint and then decreasing, yet still retaining an enormous negative value until it almost reaches us. In fine, any particular case of receding motion is perfectly reversible and may, as such, be represented among the stars. But enough has now been said against that mythical "divergence towards the future."

To proceed with our subject, notice for the sequel that eq. (3) assumes for $\gamma \doteq 1$ ($v \doteq 0$) the simple form

$$\frac{\kappa}{c} \frac{d(2\sigma)}{dt} = \pm \sin 2\sigma, \quad . \quad . \quad . \quad (3_0)$$

and similarly (4),

$$\frac{R^2}{c^2} \frac{d^2(4\sigma)}{dt^2} = \sin 4\sigma. \quad . \quad . \quad . \quad . \quad (4_0)$$

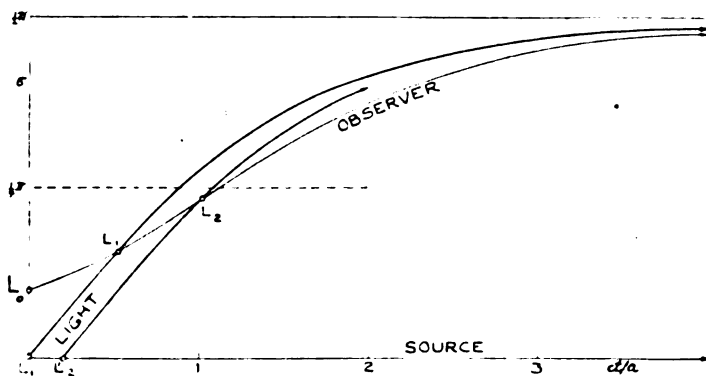
The equation (3₀) as well as (3) can at once be integrated in terms of trigonometric functions, but their integral forms will not even be needed for the problem in hand. In fact, reserving $r=0$ for the world-line L' of the star, let the observer's world-line L be any of the geodesics (3), i. e.,

$$\frac{ct}{R} = \int_{\sigma_0}^{\sigma} \frac{\sec \sigma \, d\sigma}{\sqrt{1 - \cos^2 \sigma / \gamma^2}} \cdot \cdot \cdot \cdot \cdot \quad (L)$$

The line representing the star's light signal emitted from L_1' , say at the instant $t = \alpha$, is

$$\frac{c}{R}(t-\alpha) = \int_0^\sigma \sec \sigma \, d\sigma.$$

Fig. 1.



The world-point L_1 being the intersection of L with this line, its coordinates r, t are determined by the last two equations. The relations are represented on the figure, which is drawn correctly for the sub-case $\gamma=1$, and for

a receding motion *. Imagine the last two equations solved for t , σ and differentiated with respect to α , another signal being sent, from L_2' , at $t = \alpha + d\alpha$. Then

$$c(dt - d\alpha) = \sec \sigma \cdot dr, \quad cdt = \frac{\sec \sigma \cdot dr}{\sqrt{1 - \cos^2 \sigma / \gamma^2}},$$

two equations for cdt and dr , the components of the element $L_1 L_2$ or ds in terms of $cd\alpha = ds'$, the line-element of the source. Solving these and substituting in $ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - dr^2$, we have the required ratio of proper times,

$$\frac{ds}{ds'} = \frac{\cos^2 \sigma / \gamma}{1 \pm \sqrt{1 - \cos^2 \sigma / \gamma^2}} = \gamma [1 \pm \sqrt{\text{idem}}].$$

Whence, by (2), the required formula for the complete Doppler effect,

$$D = \gamma \left[1 \pm \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2}} \right] - 1, \quad . . . \quad (5)$$

where $r = R\sigma$ is the observer's distance from the star at the moment of receiving its light. For, referring to the figure, σ was the ordinate of L_1 . The distance σ_0 at the moment of emission would be given by $L_1' L_0$ and is readily expressed in terms of σ . But the latter enters in a much simpler way into the expression of the Doppler effect, and will therefore be retained throughout the investigation. The upper sign in (5) holds for a receding, and the lower for an approaching star. We may write equivalently, by (3),

$$D = \gamma \left[1 \pm \frac{v}{c} \sec \sigma \right] - 1,$$

* This figure is also instructive in another way. It shows that the geodesics $\gamma = 1$, such as the "observer's" line $L_1 L_2$, have an inflexion-point at $\sigma = \frac{1}{2}\pi$. There the relative velocity reaches the maximum $c/2$, and the acceleration is changed from repulsive to attractive. Again, it exhibits the light-lines $L_1' L_1$, $L_2' L_1$ as asymptotic to the polar $\sigma = \frac{1}{2}\pi$. If, therefore, the observer happens to be at the polar of the star, and *vice versa*, the ratio ds/ds' of the corresponding segments ($L_1 L_2$ and $L_1' L_2'$) need not vanish, but is, to begin with, indeterminate. It acquires a definite value only when considered as the limit for a geodesic, such as $L_1 L_2$, tending to the polar, and then the limiting value of the ratio is either 2 or zero, according as we approach the line $\sigma = \frac{1}{2}\pi$ through geodesics representing a receding or an approaching motion, respectively. This disposes of the prejudice, repeated after de Sitter by all authors, as to the "complete standstill" at the observer's polar, derived hastily from (1) by putting $\sigma = \frac{1}{2}\pi$. The "standstill" exists only analytically when judged by the coordinate-time t . It disappears when we estimate the succession of events at the polar by the ratio based on light-signals, the only means of knowing anything about these events.

which, apart from $\sec \sigma$, will strike the reader as a more familiar form.

Formula (5) holds rigorously, for any value of the integration constant β entering through γ which, for all we know, may differ from star to star. Thus, the Doppler effect is, in general, by no means a universal function of distance alone. If we were to judge from most of the near stars, β^2 might be an exceedingly small fraction. Yet, no matter how small, it cannot in general be wholly disregarded, unless σ begins to amount to something. So much so, in fact, that for near stars it is β which plays the chief rôle, while $\cos \sigma$ can be confounded with unity, thus leading from (5) to

$$D = \sqrt{\frac{1 \pm \beta}{1 \mp \beta}} - 1,$$

the well-known formula of the special relativity theory. If here β^2 and higher terms be neglected, we are at once reduced to $D = \pm v_0/c$, which is the classical formula. It will be noticed that the equation of inertial motion, (3), gives for small σ a type of motion which is within short intervals of ct/R approximately uniform, with v_0 as velocity. In fine, as far as small-scale phenomena are concerned, Newton's law of inertia and the ordinary Doppler formula come to their rights. For somewhat more distant celestial objects both σ and β may have to be retained, under the radical, that is. In γ as factor of the bracketed expression in (5) the term β^2 can at any rate be neglected so that we are left with

$$D = \pm \sqrt{1 - \cos^2 \sigma} / \gamma^2 = \pm \sqrt{\sin^2 \sigma + \beta^2 \cos^2 \sigma}, \quad (5a)$$

or, for σ not exceeding a few degrees (which, however, will be seen to cover even all the extra-galactic objects hitherto explored), with more than sufficient accuracy,

$$D = \pm \sqrt{\sin^2 \sigma + \beta^2}. \quad (5b)$$

Here, for the great majority of intergalactic stars, both terms have to be retained (of course, with $\sin \sigma \doteq \sigma$), and the writer hopes to give some applications of this formula, in connexion with statistical considerations relating to comparatively near stars, at a future opportunity.

Meanwhile, aiming at the most remote objects of the sky, let us tentatively consider β^2 as altogether negligible in presence of unity, and even of $\sin^2 \sigma$, so that $\gamma \doteq 1$. Then

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formula (5) will assume the simple form

$$D = \pm \sin \sigma = \pm \frac{r}{c} \sec \sigma, \quad . \quad . \quad . \quad (5c)$$

the latter by (3). Notice in passing that, if a be the usual astronomical unit of length, de Sitter's parallax formula is

$$p \doteq \tan p = \frac{a}{R \sin \sigma} \quad . \quad . \quad . \quad (6)$$

so that the last formula can also be written, removing every doubt as to the physical meaning of ' r ,'

$$Dp = \pm \frac{a}{R} \quad . \quad . \quad . \quad (5d)$$

Keeping this in mind we may, however, retain the co-ordinate-distance r , especially as the larger distances are certainly not estimated by trigonometric parallaxes. At any rate, since the largest Doppler effect ever observed, namely +1800 km./sec. shown by the spiral nebula N.G.C. 584, still amounts to $D=6 \cdot 10^{-3}$ only, we may as well confound $\sin \sigma$ with σ and write

$$D = \pm \frac{r}{R} \quad . \quad . \quad . \quad (5e)$$

the coordination of signs being as before.

Now, D -values, all large enough, are reliably measured for some forty spiral nebulae. Unfortunately, however, as I am advised by Prof. Shapley, no good distance estimates of these fascinating objects are as yet available. Even in the case of the great nebula in Andromeda the distances found are so widely discrepant as 200,000 and 2800 parsecs, both estimates derived by Lundmark, quoted occasionally by Russell and by van Maanen, respectively. Jeans puts it even at 1700 parsecs only. Moreover, a single R -value derived from the data for the Andromeda nebula or any such object, even if it seemed of a reasonable order, would not, of course, speak either for or against the formula and the theory from which it was derived. A crucial test will consist in applying (5e) to a number of distant celestial objects for which tolerably reliable pairs of data r, D are available. Since the spirals do not as yet offer such an opportunity, let us turn to the globular clusters. The "radial velocities" of these systems are known only with a P.E. which it is, according to a private letter of Prof. Shapley, a fair guess to put at 25 to 50 km./sec. Yet, since their distances were rather consistently estimated, a test of our formula may be attempted on this class of celestial objects.

Shapley's paper in vol. xlix. of the *Astrophys. Journal*, p. 322, contains a table of ten globular clusters with both r and D values. In view, however, of the large probable errors of D , just mentioned, only those clusters seem worth considering whose measured radial velocities cD are not much below a hundred km. per sec. We are then left, for the present, with only seven clusters.

These give the following table, in which "radial velocities" are in km./sec., the corresponding D 's being simply their values divided by c , and r as well as the quotients $R = r : D$ are in astronomical units :—

Cluster, N.G.C.	r .	Rad. velocity.	$D, 10^5$.	$R, 10^{-12}$.
5024	38. 10^8	-170	- 57	6.7
5272	28 "	-125	- 42	6.7
6205	22 "	-300	-100	2.2
6333	50 "	+225	+ 75	6.7
6341	25 "	-160	- 53	4.7
6934	67 "	-350	-117	5.7
7078	29 "	- 95	- 32	9.1

The consistency of the figures of the last column, with a mean of

$$R = 6.0 \cdot 10^{12},$$

is, perhaps apart from the third item, surprisingly close, and in view of the large P.E. of the measured spectroscopic shifts (due to the very low dispersion necessary to photograph these objects at all) even better than one would feel entitled to expect. It goes without saying that many more data would be desirable before forming a final judgment. Yet, this little table, as it stands, seems encouraging, as speaking rather in favour of formula (5 e) and thus also for de Sitter's cosmology. It will be well to remember that the early determinations of the electronic e , for instance, differed from each other not less than these seven values of the curvature invariant of space-time. Again, very much as in the case of the electronic and other "universal constants," the knowledge of R in itself is not so important as the law which is implied by the consistency of the several R -values. This law, subject, of course, to many further tests, may be concisely formulated, in terms of physical magnitudes alone, as follows :—

The product of the numerical value of the Doppler effect into the parallax of a distant star is a constant, viz. the smallest parallax possible.

For, according to the parallax formula (6), a/R is precisely

this minimum parallax p_m , attained at the polar, so that the law, yet to be tested, can be written

$$Dp = \pm p_m \dots \dots \dots (7)$$

With the above value of R we should have $p_m = \frac{1}{6} 10^{-12}$ radians or $3''.44 \cdot 10^{-8}$.

To the meagre table upon which this provisional value is based but two more items can for the present be added. The Lesser Magellanic Cloud shows an effect of $+150$ km./sec. According to Hertzsprung its distance exceeds 10,000 parsecs, while Shapley's more recent estimate is 20,500 parsecs, which may here be adopted. The radial velocity of the Greater Magellanic Cloud is, according to Wilson, $+276$ km./sec., and its distance, according to Shapley, 61,000 light-years*. Thus, by (5e), we have

$$\text{from the Lesser Cloud} \dots R = 8.2 \cdot 10^{12},$$

$$\text{and from the Greater Cloud} \dots R = 4.2 \cdot 10^{12},$$

not clashing with the values derived from the globular clusters. The mean of all the nine values is

$$R = 6.05 \cdot 10^{12},$$

not differing materially from the previous one.

It is hoped that a further extension of the list, which may either discredit or strengthen the proposed formula, will soon become possible.

Returning for a moment to the spiral nebulae, for which no independent distance estimates will soon be available, we may provisionally adopt the value $R = 6 \cdot 10^{12}$ in order to obtain a preliminary idea of their distance, putting, that is, in astronomical units,

$$r = 6 \cdot 10^{12} |D|.$$

Thus, for instance, the Andromeda nebula, for which Slipher finds -300 and Pease -316 km./sec., would have to be placed at a distance of 6.0 to $6.3 \cdot 10^9$ astr. units, or, in round figures, 30,000 parsecs, which seems to fall between the extreme rough estimates occasionally quoted. The most distant spiral thus far explored would be N.G.C. 584 which shows a "radial velocity" of $+1800$ km./sec. or $D = 6 \cdot 10^{-3}$, the greatest effect ever recorded. This nebula would be placed at a distance

$$r = 3.6 \cdot 10^{10}$$

or 180,000 parsecs. Huge as this may seem, it will be

* R. E. Wilson, 'Publications of the Lick Observatory,' vol. xiii, part v, p. 187 (1918). Harlow Shapley, *Astroph. Journ.* xlix, p. 322 (1919).

remembered that Shapley's latest estimate of the semi-diameter of our galaxy is only four times smaller. Next would come the spiral N.G.C. 936, with the (doubtful) effect $+1300$ km./sec., at a distance $r=2.6 \cdot 10^{16}$. Similarly for the remaining spirals tabulated by Slipher and given in Eddington's book. Whether these estimates will or will not fit into the general scheme of modern galactic and extra-galactic astronomy, is not known to me and must be left to the scrutiny of the specialists.

The very probable existence of a large number of galaxies similar to (though, according to van Maanen, not many as large as) our own galaxy would not clash with such a world radius as $6 \cdot 10^{12}$. In fact the total volume of the elliptic space, which is but a particularly simple section of de Sitter's fourfold, being $V=\pi^2 R^3$, and our own galaxy being roughly representable as an ellipsoid of semiaxes $A=B=10 \text{ ('} = 9.5 \cdot 10^9 \text{ astr. units)}$, its volume would bear to V , very nearly, the ratio

$$V_g/V = \frac{2}{15\pi} \left(\frac{A}{R}\right)^2,$$

which, with $R=6 \cdot 10^{12}$, is as small as $\frac{1}{6} 10^{-9}$. There would thus be room enough for hundreds of millions of such systems with ample intergalactic spaces. Moreover, when judged by the time succession of light-messages from further and further objects, up to our polar, our universe would to all purposes be rigorously infinite, thus not thwarting even the most sublime of our cosmic emotions, to use a word and a concept dear to W. K. Clifford.

My thanks are due to Prof. Harlow Shapley, of the Harvard College Observatory, for aiding me most kindly in extending that minute table.

Rochester, N. Y.,
January 23, 1924.

Note added in Proof reading, March 15, 1924.

The list of nine given above can just be supplemented by one more R -value. For the globular cluster Messier 12, or N.G.C. 6218, Sanford (Mt. Wilson Annual Report for 1919, p. 250) has found $vD = +160$ km./sec., and its distance is estimated by Shapley at 12,400 parsecs, whence, by (5 e).

$$R = 4.8 \cdot 10^{12} \text{ astr. units.}$$

It will be noticed that this cluster, being placed at much the

same distance as our previous N.G.C. 6341 (12,300 parsecs) shows a Doppler effect of the opposite sign, but of just the same absolute value, in agreement with (5e).

The ten R -values thus far obtained from the clusters N.G.C. 5024, 5272, 6205, 6333, 6341, 6934, 7078, 6218 and the Lesser and the Greater Magellanic Clouds are, respectively,

6.7 6.7 2.2 6.7 4.7 5.7 9.1 4.8 ; 8.2 4.2 . 10^{12} astr. units.

If, as was tentatively assumed, β^2 is for all these objects actually negligible in presence of σ^2 , the differences between these ten R -values can be attributed to the observation errors of the data, and we may strike an average of the ten determinations, which would give $R=5.9 \cdot 10^{12}$ or, in round figures, *six million million* astr. units.

If, on the other hand, we return to the more accurate formula (5b), and if each of the ten pairs of observations is considered to be materially correct, we are, in our present ignorance of the individual β 's, entitled only to conclude that

$$R = r / \sqrt{D^2 - \beta^2} \geq r : D,$$

that is, $R \geq 9.1 \cdot 10^{12}$, with a strong likelihood, however, that R is not much greater than 10^{13} . (Cf. in this connexion a letter to the Editor of 'Nature,' dated March 3.)

A possible method of clinching the question, *i. e.* of determining β and σ separately, and thus also of deriving the radius R from less distant stars, for which D and r can be more accurately measured, will be described in a later communication.

XC. An All-metal High-vacuum Pump System. By
IVOR BACKHURST, M.Sc., and G. W. C. KAYE, O.B.E.,
M.A., D.Sc. (From the National Physical Laboratory *.)

I. INTRODUCTORY.

THE two conspicuous advances in the more recent history of high-vacuum production are doubtless (a) the use of liquid air and charcoal, a method due, as is well known, to the late Sir James Dewar; and (b) the invention of the condensation pump by Langmuir.

The charcoal and liquid air method was the standard method of producing high vacua, from its discovery in 1904 until the development of the condensation pump in 1916.

* Communicated by the Director.

The charcoal method is capable of affording extreme vacua, but at the lower pressures the method is normally slower than the condensation pump.

The different types of high-vacuum pumps available at the present time may be conveniently divided into four classes:—(1) Oil-sealed pumps; (2) Mercury-sealed pumps; (3) High-speed mechanical pumps; (4) Mercury-vapour pumps.

(1) Oil-sealed Pumps.

These are mechanical and fall into two divisions:—

(a) *Piston*.—The earlier vacuum pumps were all of the piston type and in the Geryk¹ pattern are still much used.

(b) *Rotary*.—The rotary oil pumps first designed by Gaede², although probably foremost for medium vacuum work, are not generally adopted for pressures above 1 mm. or so, but rather are used to obtain pressures of the order of 0.001 mm. when supported by a piston-pump capable of reducing the pressure directly from atmospheric to about 0.1 to 2 mm. The rotary pumps are, however, slow in dealing with vapours and the oil is apt to become contaminated. The vibration they occasion is considerable, and it is important to protect them against water vapour by the use of drying-tubes. The provision of a by-pass tap and a trap is advisable to assist in preventing overflow of oil in the event of the back-pressure rising or a sudden leak developing in the apparatus to be exhausted. The speed, as defined by Gaede (see p. 925), is from 100 to 150 c.c./sec.

(2) Mercury-sealed Pumps.

The simplest pump of the mercury-sealed type is the *Sprengel*³ which depends on liquid-jet action and, according to Kahlbaum, is capable of reaching a pressure lower than 10^{-5} mm.

The *Töpler*⁴ pump, a simple piston-pump in which mercury is used as the piston, is capable of doing nearly as well, and was formerly almost exclusively employed in laboratories devoted to electric discharge-tube research. Both this and the Sprengel pump require constant attention and are extremely slow and, on this account, they are now comparatively little used.

The *Gaede*⁵ rotary mercury-pump, consisting essentially of an Archimedean screw having its axis horizontal and immersed in mercury to a level somewhat above the axis,

is faster than either of the above and requires little attention when motor driven. Its speed is about 100 c.c./sec. It requires a fore-vacuum of about 10 mm. and a by-pass for the supporting pump is necessary. Vapours are pumped very slowly and drying-tubes are required. Although the rotary mercury-pump has been used in many modified forms since it was designed in 1905, it has given place in factory work during the last few years to the rotary oil-pump.

(3) *High-speed Molecular Pumps.*

The molecular pump, invented by Gaede⁶, consists of a grooved cylinder, designed to rotate at about 10,000 revs./min. with a clearance of the order of 0.01 cm. inside a cylindrical casing in which are narrow radial extensions protruding into the grooves. On either side of the extensions are inlet and outlet ports connected in series fashion. The pumping action depends on the fact that in confined spaces at low pressures the collisions of a molecule with the boundary walls are much more frequent than with other molecules. It follows that if one of the walls is in motion, the molecules tend to take up rapidly the direction of this motion. At low pressures the pump maintains a definite ratio between the pressures on either side of it, the value of the ratio for a given speed of rotation and the same gas or vapour depending only on the dimensions of the pump. The value of the ratio may be as much as 100,000. The speed of pumping for air may reach 1400 c.c./sec. at about 0.01 mm. pressure, but falls off rapidly at lower pressures.

* A type of molecular pump, incorporating a number of improvements, has been designed by Holweck¹³.

(4) *Mercury-vapour Pumps.*

(a) *Diffusion pump.*

The mercury-vapour diffusion pump, also first designed by Gaede⁷, is a true diffusion pump, mercury-vapour and air diffusing through a narrow slit in *opposite* directions. The vapour, after passing the slit, is condensed and returned to the boiler, while the air passing through to the opposite side of the slit is carried away by the supporting pump. The high vacuum is thus on the condenser side of the slit. A great disadvantage is that for efficient operation the pressure of the vapour at the slit must be only slightly in excess of that

* Added January 1924.

of the fore-vacuum, so that the temperature of the mercury must be carefully regulated. The pump is also slow, the speed not generally reaching 100 c.c./sec. The advantages of the diffusion pump are that there is no theoretical limit to the lowest pressure attainable, and also that vapours are dealt with as well as gases. These advantages are, however, common to all the various forms of mercury-vapour pumps.

(b) *Condensation pumps.*

In the form of "condensation" pump devised by Langmuir⁸, a blast of mercury vapour is directed tangentially against a water-cooled surface, along which the gas to be pumped is driven. The action depends on the energy of the mercury molecules "reflected" from the cooled surface being too small and non-directive to interfere with the direct blast. The pump is extremely fast, its speed being 3000–4000 c.c./sec. Moreover, the temperature-control is not critical. A fore-vacuum of 0.001 to 0.01 mm. is generally used, the upper limit being about 0.1 mm., and, as already mentioned, the theoretical limit of the pressure obtainable is zero.

Several modifications of the Langmuir type of pump, making use of the jet principle (as in a steam ejector), have proved very successful, such as Crawford's⁹ parallel-jet pump, and the two-stage pumps of Stimson¹⁰ and Volmer¹¹, on the rapidity of which we have no quantitative information. In a two-stage pump the pressure of the fore-vacuum need not be less than a few millimetres, so that a simple piston oil-pump is the only auxiliary required. In each of these modifications the conditions require a fine annular clearance round the jet. So far, jet pumps, owing to difficulties in design, have been constructed only of glass or silica and have not, to our knowledge, been made of metal. The fragility of a glass or silica pump system, while not so important in a research laboratory, is, however, an admitted disadvantage from the industrial point of view.

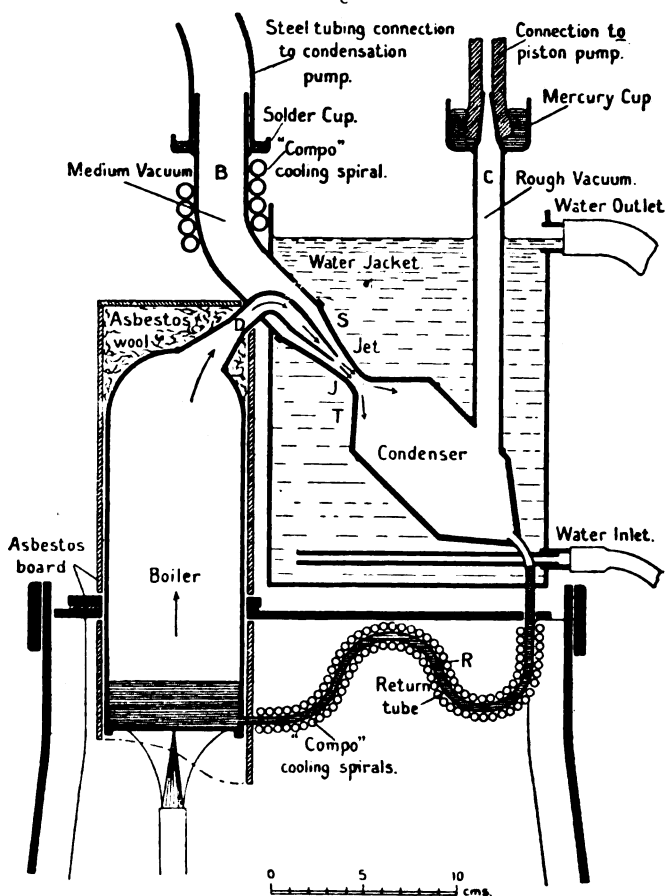
II. DESCRIPTION OF APPARATUS.

The pump system about to be described is of the two-stage type, constructed wholly of metal and consisting of (1) a mercury-vapour jet pump in series with (2) a mercury-vapour condensation pump. It may perhaps be urged that there is no real demarcation between the two types of pumps, but the terms are convenient.

(1) *Mercury-vapour Jet Pump.*

The essential features of the first-stage vapour pump are shown in fig. 1, which is drawn to scale and is almost self-explanatory. The pump is made of steel, mainly from tubing, and all joints are welded*. Our experience is that,

Fig. 1.



Mercury-vapour Jet Pump.

unless welding is carried out by a welder fully accustomed to this class of work, the resulting joints are apt to be porous. We have found that the best remedy for this is thorough nickel-plating.

The boiler is lagged with asbestos board and wool. The

* Brazing is objectionable since it causes gradual contamination of the mercury, while the brazing itself is liable to become porous.

condenser is surrounded by a water-jacket, as shown, and in addition it was found essential to cool the return tube R, which can be conveniently done by the use of coils of "compo" tubing. Two or three turns of cooling spiral are also wound round the tube B on the medium vacuum side. When the pressure in the pump has been reduced to 4 mm. or less, by means of a piston-pump, the jet pump is set in operation by turning on the circulating water and setting a small Bunsen burner under the boiler, the latter containing about $1\frac{1}{2}$ kgms. of mercury. A pointed flame prevents excessive bumping, and in practice a $\frac{3}{8}$ inch diameter Bunsen burner, working under a gas pressure of 4 cm. of water, is found to be convenient. If the pressure at C is about 2 mm., the pressure at B will be reduced to less than 0.001 mm.

The action of the pump is as follows:—Vapour leaves the boiler by the tube D, which is streamlined as far as is practicable, and decreases in cross-section up to the nozzle at J. The mercury vapour issues as a divergent jet, the outer portions of which strike against the water-cooled throat T. Gas or vapour diffusing from the annular space S is caught in the jet and carried into the condenser, and so to the piston pump, while the condensed mercury returns to the boiler through the tube R. The action of the pump is mainly that of the ejector, but utilizes also the condensation principle.

In determining the dimensions of the jet pump, the following points have received attention:—

(1) The boiler is designed to be of sufficient cross-section to allow an adequate rate of evaporation without recourse to excessive temperature and vapour pressure.

(2) The height of the boiler is determined by the necessity of allowing for:—

- (a) Vertical height of the condenser.
- (b) Difference of level between mercury in return tube near condenser and mercury in the boiler.
- (c) Sufficient depth of mercury in the boiler.

(3) The tube leading to the nozzle and the nozzle itself are everywhere streamlined as far as practicable.

(4) The slope of the nozzle, throat, and condenser is everywhere arranged to be sufficient to ensure the flow of condensed mercury to the return tube.

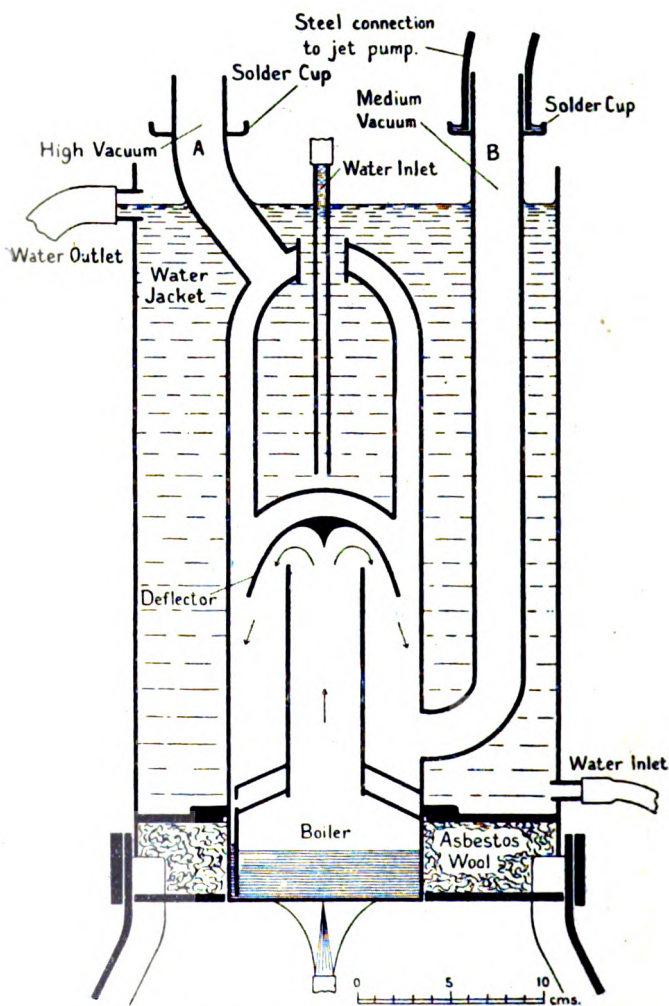
(5) The clearance between the throat and nozzle has to be small, although the cross-sectional area of the nozzle could be increased considerably beyond that shown, providing that the boiler were capable of supplying a sufficient stream of vapour.

(6) The neck has to be prolonged sufficiently beyond the nozzle to avoid the return of air past the jet.

(7) The water-cooling is extended well back behind the mouth of the nozzle to promote efficient operation.

(8) The surface-area and volume of the condenser and the cross-section of the return tube have to be adequate.

Fig. 2.



Mercury-vapour Condensation Pump.

(2) *Mercury-vapour Condensation Pump.*

The second-stage vapour pump is shown to scale in fig. 2, and is substantially as designed by Langmuir. It is made of steel tubing, the joints being welded and the whole nickel-plated. Since the pressure of the vacuum produced by the jet pump is as low as 0.001 mm., it is possible for the clearance between the deflector and the surrounding pump cylinder to be made wide, over 1 cm., so that the high speeds possible with this type of pump can be secured to advantage. An interior-cooler, which is provided in the upper half of the pump cylinder, effectively increases the area of condensation.

The two pumps are connected by steel tubing of $1\frac{1}{4}$ inch bore, the joints being made conveniently and quickly by the use of solder cups, which have been found to behave satisfactorily over a period of some months.

III. SPEED OF THE PUMP SYSTEM.

The speed of a vacuum pump has been defined by Gaede in the following way :—

If at any instant (t) the pressure in the vessel being exhausted is p , then

$$-\frac{dp}{dt} = kp,$$

where k is a constant over a limited range of p . Since the time taken for exhaustion varies inversely as $\sqrt{V}$, the volume being exhausted, we can write

$$-\frac{dp}{dt} = \frac{S}{V} \cdot p,$$

or, on integration,

$$S = \frac{V}{t_2 - t_1} \log_e \frac{p_1}{p_2}.$$

If the vessel being exhausted is immediately adjacent to the pump, then S is the speed of the pump and is measured in c.c./sec. of gas at the pressure obtaining at the instant considered.

Determinations have been made as to the way in which S varies with the pressure for the metal-pump combination under discussion. The values were obtained by means of a constant flow apparatus, using Knudsen's¹² general equation

$$F = aP + b \frac{(1 + c_1 P)}{(1 + c_2 P)}$$

for the flow of a gas through tubing of circular cross-section. F is the flow in c.c./sec., measured at a pressure

of 1 dyne/cm.² for 1 dyne/cm.² pressure-difference between the ends of the tube; P is the average pressure in the tube in dynes/cm.², and a , b , c_1 , and c_2 are constants for a given tube when air is the gas considered.

The flow-tube employed connected two spherical bulbs of about 8 cm. diameter, one of which was joined to the low-pressure end of the pump system and the other was connected to the high-pressure end of the pump system through a drying-tube. In this way the pumps were used to circulate dry air through the flow-tube, without occasioning any flow to the supporting oil pump, so that the latter in no way contributed to the pump-speed measured by this method. The pressures in the bulbs were read, as soon as a steady state obtained, by means of two McLeod gauges connected one to each bulb. For pressures less than about 150 dynes/cm.² the flow-tube was 42 cm. long and 1 cm. diameter; for higher pressures the flow-tube was 36 cm. long and 0.5 cm. diameter. The connecting tubing between the low-pressure bulb and the pump system was 14 cm. long and 2.71 cm. diameter.

To consider the case of the flow-tube for the lower pressures, the flow Q through the tube under a pressure-difference ($p_1 - p_2$) is given by the equation

$$Q = F(p_1 - p_2) = \left\{ 3.24 P + 279.2 \frac{(1 + 0.1903 P)}{(1 + 0.2360 P)} \right\} (p_1 - p_2).$$

Also $Q = S'p_2$, where S' measures in c.c./sec. of air at pressure p_2 the pumping speed at pressure p_2 of the system comprising the pumps and connecting tube. The true pump speed S is obtained from this, as follows:—

If the pressure at the pump end of the connecting tube is p_3 , and F' is the flow through the tube for unit pressure-difference at its ends, then we have

$$Q = F'(p_2 - p_3) = S'p_2 = Sp_3,$$

or

$$\frac{1}{S} = \frac{1}{S'} - \frac{1}{F'}.$$

F' can be obtained from Knudsen's equation, being in this case

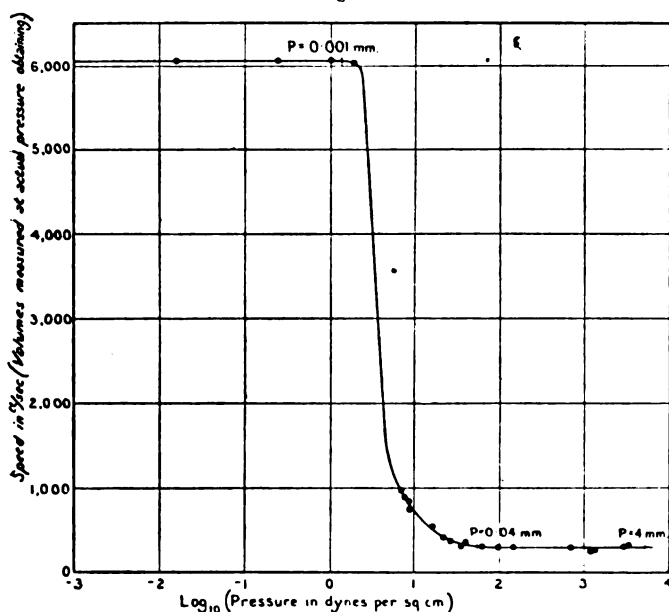
$$F' = 524 P' + 13730 \frac{(1 + 0.516 P')}{(1 + 0.639 P')}.$$

* Q is measured in c.c. per sec., the volume measurements being referred to a pressure of 1 dyne/cm.²

For low values of P' , F' is nearly constant, while for higher values $\frac{1}{F'}$ is very small compared with $\frac{1}{S'}$, so that P' may be taken as being equal to p_2 without making appreciable error.

In this way values of S have been found for various values of P' . In seeking a graphical representation of the results, it is more convenient and illuminating to plot S against $\log P'$, and this has been done in fig. 3. The graph

Fig. 3.



clearly shows that the speed of the pump system at pressures from 4 mm. to 0.03 mm. is constant and equal to 300 c.c./sec., this being due to the jet pump alone. Below this pressure the condensation pump begins to operate and the speed increases rapidly to 6000 cc./sec. at 0.0015 mm. pressure, and remains constant at this value for lower pressures. This may be regarded as a minimum figure which normally obtains without undue care as to the conditions. However, by careful adjustment of the temperature for any particular pressure, it has been found possible to increase this value to as much as 10,000 c.c./sec.

IV. ADVANTAGES OF THE PUMP SYSTEM.

The advantages of this type of two-stage pump system may be summarized as follows :—

- (1) The speed of pumping is extremely high.
- (2) Pressures of the order of 10^{-6} mm. or less (*i.e.* the lowest pressures obtainable by any type of pump) are possible when supported by a simple piston oil pump.
- (3) There are no moving parts, so that there is a complete absence of vibration, mechanical wear, and noise.
- (4) Vapours are pumped as efficiently as permanent gases.
- (5) No drying or other reagents are required.
- (6) The system is very robust and dependable since glasswork and rubber joints are eliminated.
- (7) The temperature control is not critical and the system requires little or no attention while running.
- (8) There is a continuous passage from supporting pump to high vacuum, so that no by-pass is necessary. The occurrence of a sudden leak in the apparatus under exhaustion or the failure of the supporting piston-pump will not occasion the overflow of liquid from the pumping system.
- (9) The running costs are low.
- (10) The weight is much less than that of the usual rotary oil-pump combination, so that the system is more readily portable when occasion demands.

SUMMARY.

A two-stage mercury-vapour pump system constructed wholly of steel has been devised, which consists of a jet-pump and a condensation-pump in series. The system requires a fore-vacuum of 4 mm. to afford the highest vacua obtainable by a mercury condensation pump. There are no moving parts, vapours are pumped as efficiently as gases, no drying reagents are required, and glass work and rubber joints are eliminated. Above 0.03 mm. pressure the speed (using Gaede's definition) is constant at 300 c.c./sec.; below this pressure the speed increases rapidly to a constant value of 6000 c.c./sec.

A short resumé of existing vacuum pumps is given in this paper. The following approximate speeds are quoted :—

	c.c./sec.
Gaede rotary oil-pump	100-150
Gaede rotary mercury-pump ...	100
Gaede diffusion pump	100
Gaede molecular pump	1400 (max.)
Langmuir condensation pump ...	3000-4000

The all-metal pump system described in this paper, which has in the main been designed and tested by I. Backhurst, was made in the workshops of the National Physical Laboratory. Much help in the construction and testing of the pumps has been given by Mr. J. Balmanno and Mr. W. H. Sewell, of the Observer Staff of the Laboratory.

The investigation, which is being continued, has been carried out in part in connexion with work in progress for the Radio Research Board of the Department of Scientific and Industrial Research.

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A good bibliography is contained in a series of articles in the 'General Electric Review' by Dushman on "The Production and Measurement of High Vacua," commencing in vol. xxiii. p. 493 (1920), which includes most of the earlier references given above. These articles are now published in book-form under the above title.

In Glazebrook's 'Dictionary of Applied Physics,' vol. i. p. 24, a useful list of references will also be found.

XCI. *Geometrical Note on de Sitter's World.*

By P. DU VAL*.

THE Hyperbolic world of four dimensions is describable by means of Wierstrassian homogeneous coordinates x, y_1, y_2, y_3, y_4 ; a point is determined by the ratios of these, and for a real point the ratios are all real, so that if x is real all the coordinates are real. The manifold of real points is divided into three portions by means of the function $x^2 - \Sigma(y^2)$. Points for which—all the coordinates being real— $x^2 > \Sigma(y^2)$ are actual, those for which $x^2 = \Sigma(y^2)$ are absolute, those for which $x^2 < \Sigma(y^2)$ are ideal.

In discussing the actual field of this world, it is convenient to subject the coordinates to the condition $x^2 - \Sigma(y^2) = 1$. With this convention we find that the linear element ds between two infinitesimally neighbouring points is given by

$$ds^2 = \Sigma(dy^2) - dx^2.$$

For a discussion of the ideal field of this world it is manifestly more convenient to make our restriction $x^2 - \Sigma(y^2) = -1$. This is equivalent to multiplying by i each of the coordinates obtained by the former restriction; the infinitesimal increments of the coordinates are, of course, multiplied by i also, and the square of the linear element accordingly becomes

$$ds^2 = dx^2 - \Sigma(dy^2).$$

Since our five coordinates satisfy an equation, we can express them in terms of four parameters so that this equation becomes an identity. Let us put

$$\begin{aligned} x &= \cos \chi \sinh t, \\ y_1 &= \cos \chi \cosh t, \\ y_2 &= \sin \chi \cos \theta, \\ y_3 &= \sin \chi \sin \theta \cos \phi, \\ y_4 &= \sin \chi \sin \theta \sin \phi. \end{aligned}$$

Then $x^2 - \Sigma(y^2) = -1$ identically. To every set of values (t, χ, θ, ϕ) correspond determinate values of (x, y_1, y_2, y_3, y_4) , except where $\chi = \pm \frac{\pi}{2}$, $t = \pm \infty$ which give $y_1 = 0$, $x = 0 \times \infty$, and the ratios of y_2, y_3, y_4 determined by θ, ϕ . There are more cases in which (x, y_1, y_2, y_3, y_4) leave some of (t, χ, θ, ϕ) indeterminate; thus $y_3 = y_4 = 0$ makes $\theta = 0$, ϕ indeterminate;

* Communicated by the Author.

$y_2=y_3=y_4=0$ makes $\chi=0$, θ and ϕ both indeterminate ;
 $x=y_1=0$ makes $\chi=\pm\frac{\pi}{2}$, t indeterminate.

In terms of (t, χ, θ, ϕ) the expression for the linear element becomes

$$ds^2 = \cos^2 \chi dt^2 - \{d\chi^2 + \sin^2 \chi (d\theta^2 + \sin^2 \theta d\phi^2)\}$$

which is the expression for the linear element in de Sitter's spherical world. Since a change in sign of all the Wierstrassian coordinates leaves them still referring to the same point, χ is indeterminate to the extent of an additive π , θ and t to the extent of a simultaneous additive π and $i\pi$ respectively. Thus it is the elliptic case, not the spherical, of de Sitter's world which is the ideal field of the Hyperbolic world.

The curve in the Hyperbolic world along which $\int ds$ between any two points is stationary for all infinitesimal deformations which vanish at the two end-points, is the straight line. Thus in de Sitter's world we can say that the world-line of a particle is a straight line. If the line joining two points A, B meet the absolute $x^2 = \Sigma(y^2)$ in I_1, I_2 , the distance $\overline{AB} = \frac{1}{2} \log R(ABI_1I_2)$; so that if I_1, I_2 are real distinct points $\overline{AB}$ is real, if I_1, I_2 coincide $\overline{AB}=0$, if I_1, I_2 are conjugate complex points $\overline{AB}$ is purely imaginary. That is, lines through any given point are either

- (i.) timelike, *i.e.* containing real intervals ; they are secants of the absolute ;
- (ii.) minimal, *i.e.* containing zero intervals between non-coincident points ; they are tangents of the absolute ;
- (iii.) spacelike, *i.e.* containing purely imaginary intervals between real points ; they are non-secants of the absolute.

The whole world cannot be described by real values of (t, θ, ϕ, χ) . We may take any timelike straight line as $y_2=y_3=y_4=0$, *i.e.* as the world-line of an observer who considers himself permanently at rest at the origin of elliptic-polar coordinates (χ, θ, ϕ) in space. We find that $t=s$ along this line ; and that every partition $t = \text{const.}$ is perpendicular to this. Also, since

$$x \cosh t = y_1 \sinh t,$$

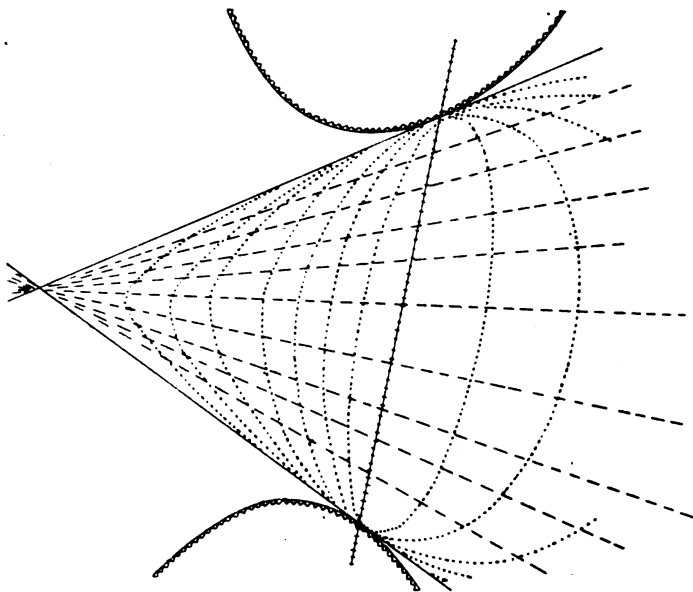
$t = \text{const.}$ is a flat space, *i.e.* one which if it contains two points of a straight line contains the whole of it. These

spaces all intersect in the horizon, $x=y_1=0$, which is the polar plane of $y_2=y_3=y_4=0$. Now the tangent spaces to the absolute at its intersections with $y_2=y_3=y_4=0$ meet in this polar plane, and are thus the spaces which join the plane $x=y_1=0$ respectively to the points $(y_2=y_3=y_4=0, x-y_1=0)$ and $(y_2=y_3=y_4=0, x+y_1=0)$ respectively. These two points are $t=\pm\infty$ at the origin of space. But we have seen that the space joining $x=y_1=0$ to the point $t=t_1$ at the origin of space, is the locus $t=t_1$; thus the loci $t=\pm\infty$ are the tangent planes to the absolute at its intersections with $y_2=y_3=y_4=0$. The locus $\chi=\text{const.}$ is given by

$$x^2 - y_1^2 = \cos^2 \chi (x^2 - \Sigma(y^2)) ;$$

this is a quadric which meets the absolute in the same surface as does the locus $x^2 - y_1^2 = 0$, or $t = \pm\infty$, which we have seen

Fig. 1.



to consist of two flat spaces, both touching the absolute. Thus the surface of intersection reduces to two conjugate points—the points of tangency. Thus $\chi=\text{const.}$ is an equidistant-locus whose axis is the line joining these two points of tangency, *i. e.* $y_2=y_3=y_4=0$.

Fig. 1 represents a plane section of the world, given by determinate values of θ, ϕ , in the Cayley-Klein projection. The absolute is shown by — — —, the world-line of the

origin by +++++, the loci $t = \pm \infty$ by ———, other time partitions by -----, and the space partitions $\chi = \text{const.}$ by The plane meets the "horizon" in a point in which the traces of all the time partitions are concurrent.

The motion of a particle in this space is very simple—its world-line is a straight line. Now the equations of a straight line are

$$y_2 = A_1 y_1 + A_2 x,$$

$$y_3 = B_1 y_1 + B_2 x,$$

$$y_4 = C_1 y_1 + C_2 x,$$

$$i. e., \quad \tan \chi \cos \theta = A_1 \cosh t + A_2 \sinh t,$$

$$\tan \chi \sin \theta \cos \phi = B_1 \cosh t + B_2 \sinh t,$$

$$\tan \chi \sin \theta \sin \phi = C_1 \cosh t + C_2 \sinh t.$$

If the motion is restricted to be radial, *i. e.* if θ, ϕ have fixed values, we have

$$\tan \chi = A_1 \cosh t + A_2 \sinh t.$$

There are three cases of this; if $|A_1| > |A_2|$, the equation becomes

$$\tan \chi = A \cosh (t - t_0),$$

showing that the particle approaches the origin with negative acceleration till it reaches a minimum distance $\tan^{-1} A$ at time t_0 , after which it recedes. If $|A_1| < |A_2|$, we have

$$\tan \chi = A \sinh (t - t_0).$$

Here the particle approaches the origin, passes through it with minimum velocity $\frac{dx}{dt} = A$, and recedes on the other side. The limiting case

$$\tan \chi = A (\cosh t \pm \sinh t)$$

gives a particle which recedes from or approaches the origin asymptotically.

These three cases are those in which the world-lines of the origin and the moving particle intersect in the actual field, the ideal field, and the absolute respectively.

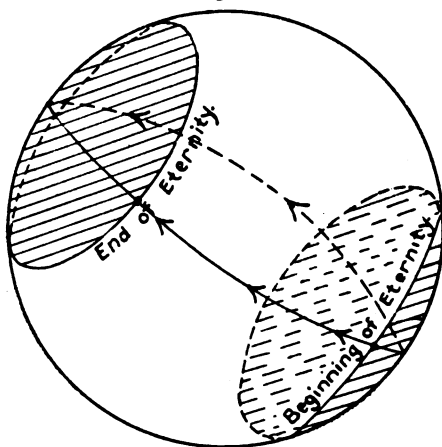
In the elliptic case, which is what most naturally arises from consideration of Hyperbolic Geometry, the absolute is a single closed curve, and every timelike line meets it in two points. There does not seem to be any particular way in which we can discriminate between $t = -\infty$ and $t = +\infty$ for an observer whose body is in that line. Certainly every observer has a consciousness which works in a definite sense along his world-line, being at every point of his life conscious

of events in the line on the negative side of him, but not on the positive side. Moreover, the light-cone (*i. e.* the cone of minimal lines) at whose vertex he is, is divided there into two sheets, the fore-cone and the after-cone, and he can see the events of the first sheet and not those of the second.

How is this clearly marked sense determined? It is absurd to suppose that each observer's sense is determined at random, for it is certain that the entire human race—whose lines are sensibly parallel—are set the same way along them.

In the spherical case this difficulty vanishes. Here the absolute consists of two distinct closed curves, which separate two distinct actual fields from an annular ideal field. The state of affairs may best be shown on a spherical surface, representing straight lines by great circles, and the absolute

Fig. 2.

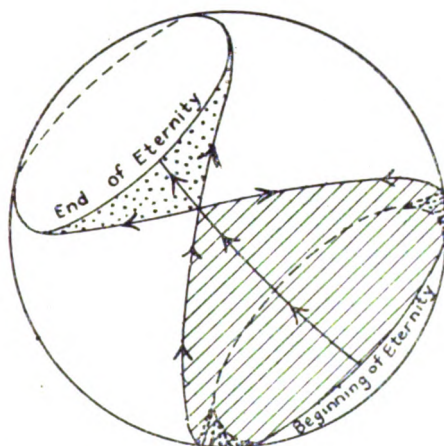


by the two branches of a spheroconic. In fig. 2 the actual fields are shaded. Every timelike line now has two actual and two ideal segments; each actual segment is bounded by two points on the same branch of the absolute, but each ideal segment is bounded by one point on each branch. The two ideal segments, being wholly distinct, are the tracks of different particles; and we may regard a world-line as consisting of one ideal segment only; with this convention we see that every world-line meets each branch of the absolute once; so that we can make the condition that all points $s = -\infty$ (s = proper-time along a world-line) lie on one branch, the beginning of eternity, and all points $s = +\infty$ on the other, the end of eternity.

Thus the phenomenon of memory may be roughly summarized by saying that an observer has some consciousness of events in his world-line between himself and the beginning of eternity, none of events on the other side of him.

A line which touches the beginning touches also the end of eternity; this is a minimal line or light-track; the two points of tangency divide it into two segments; and we must suppose light starts at the $-\infty$ point, and travels along the line both ways to the $+\infty$ point. Thus a single segment constitutes a light-track. In fig. 3 two light-tracks are shown intersecting at a point in the observer's life, which divides each of them into a fore-cone segment and an after-cone segment. The

Fig. 3.

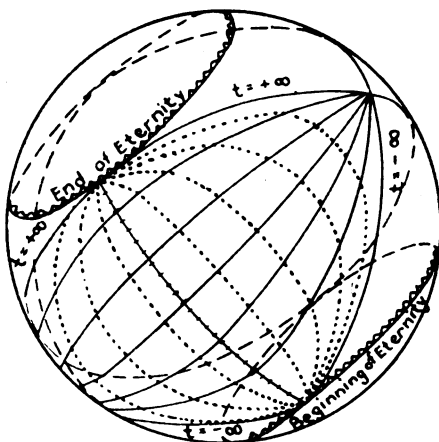


shaded area represents the events which he can see, or has already seen; the dotted, world-points from which he is visible, or will yet be visible.

Fig. 4 represents the same as fig. 1. The absolute is shown by ~~~~~, the world-line of the observer by ++++, the time partitions by ----, and the space partitions by The horizon plane now meets the plane of section in two antipodal points, $\chi = +\frac{\pi}{2}$ and $\chi = -\frac{\pi}{2}$ for the given values of (θ, ϕ) .

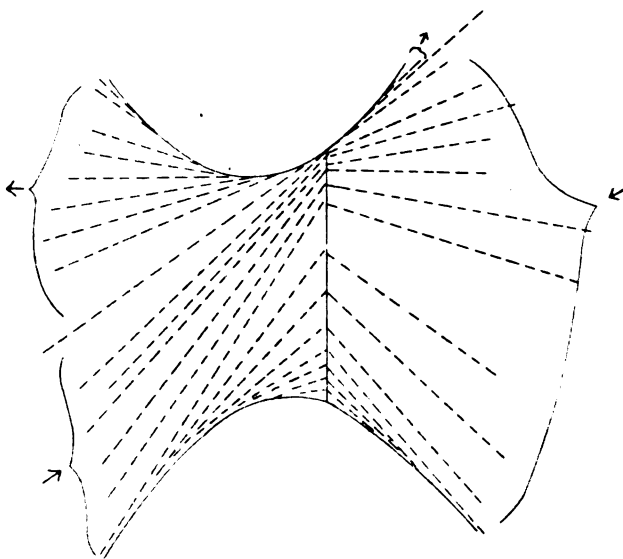
Another question of interest is, how much of the world does the observer see at one time and another during eternity? In the elliptic world he sees all of it, in the spherical world half. The same is true of the portion of the world from

Fig. 4.



which one event or another in his world-line can be seen. Fig. 5 illustrates the elliptic case in the Cayley-Klein representation.

Fig. 5.

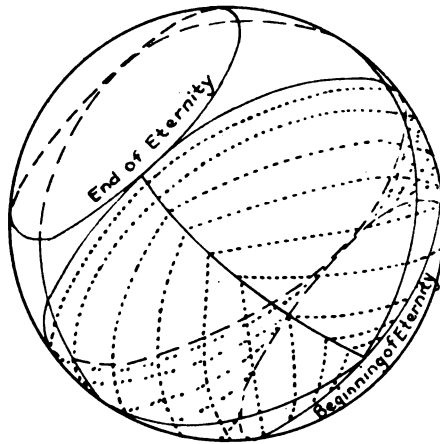


From this figure (which shows the fore-cone only, at various points of the world-line) it appears that in the elliptic world the sense in which light travels in a minimal

line is relative to the observer, *i. e.* there is no absolute distinction between fore-cone and after-cone; the observer merely, having his consciousness turned in some obscure way towards his past, sees that part of the cone which lies on the same side of him as his past. This relativity is made evident by the abrupt change in sense of the light, which occurs at the minimal $t = +\infty$. If the corresponding figure be drawn for the after-cones, it is evident that some point in the world-line is visible from everywhere in the world, and that a further discontinuity of sense in the light rays occurs at $t = -\infty$.

The spherical case is illustrated in fig. 6. The fore-cones are shown by , the absolute, the world-line, and the

Fig. 6.



minimals $t = \pm\infty$ by ———. The region covered by the fore-cones includes the coordinate field, and the two spandril-shaped regions between $t = \pm\infty$ and the beginning of eternity. Similarly, the region of the after-cones includes the coordinate field, and the other two spandrils, between $t = \pm\infty$ and the end of eternity. The field antipodal to the coordinate field is not included in either region. This field, as a matter of fact, is also described by real (t, χ, θ, ϕ) , since the antipode of (t, χ, θ, ϕ) is $(t, \chi + \pi, \theta, \phi)$. It is, however, separated from the ordinary coordinate field by the horizon, and no point in the one field is visible from any point in the other, except those of the loci $t = \pm\infty$. These two loci, as well as being flat spaces, are also pencils of light-rays; thus

light-rays diverge from $(t = -\infty, \chi = 0)$, in every direction in the space $t = -\infty$; each ray passes through a point in the horizon, and they converge to the point antipodal to $(t = -\infty, \chi = 0)$. Similarly, rays converge on $(t = +\infty, \chi = 0)$, which have all started from the antipodal point and come through the horizon. It is thus a little misleading to assert that light is arrested at the horizon. The analytical results which appear to suggest this are really expressions of the singularities which occur in the transformation from (t, χ, θ, ϕ) to (x, y_1, y_2, y_3, y_4) .

We have here two worlds to choose from as approximate representations of phenomena.

The spherical world offers a possible definition of past and future sense on a timelike world-line. On the other hand, half only of the world can come within the experience, either direct or visual, of any one observer; and it is a little problematic how far we can with meaning assert the existence of the other half.

The elliptic world has the advantage that it affords a concise description of just what is visible to one observer of infinite longevity; but it leaves to chance the discrimination between his past and his future. One would certainly be inclined to say that there was an *a priori* distinction between the two senses of time; but we must remember that our conviction of this can only refer to the earth, or at least the solar system. We have really no means of knowing that inhabitants of Sirius have not memories and eyes that work the opposite way to ours; or indeed that their memories and eyes do not work both ways at once, so that the fore-cone and after-cone have no different properties for them. As for the solar system, of course, the irregular local departures from de Sitter's metric which constitute the matter of it may be such as to bind all the particles of it together in a way that leaves sameness of sense between the world-lines of two of them definable. Thus the elliptic case is not inconceivable; and it is certainly more amusing than the spherical. The possibility—remote, it is true—of the entry into our world of someone whose memory works backwards, is to me a sufficient reason for believing in elliptic, not spherical, geometry; not to mention that projective geometry is so much simpler when two straight lines cannot meet in more than one point.

XCII. *Note on the Wave Form of the Current when an Electric Discharge is passed through Mercury Vapour.* By F. H. NEWMAN, D.Sc., A.R.C.S., Professor of Physics, University College, Exeter*.

[Plate VII.]

IT has been noticed by Pierce† that the Cooper Hewitt mercury vapour lamp will under certain conditions act as a low resistance air-gap but with greater uniformity. If the terminals of such a lamp are shunted by a condenser in series with an inductance, and a high voltage is applied to the terminals, electrical oscillations are excited in the condenser circuit which includes the condenser, inductance, and mercury lamp. As the voltage increases the condenser becomes charged, but the mercury vapour when cold is a non-conductor. At a certain voltage the resistance of the mercury vapour, due to the disappearance of the cathode resistance, breaks down, and a current passes through it. The condenser discharges through the lamp with oscillations providing that $\frac{L}{C}$ is greater than $\frac{R^2}{4}$ where L is the self-induction, C the capacity, and R the resistance of the circuit. When the voltage falls to a critical value the mercury vapour ceases to conduct and maintains its high resistance until the voltage rises again, and the process is repeated. Because of this high initial resistance about 5000 volts alternating current is required to maintain a current of about two amperes through the lamp, whereas 100 volts continuous current is sufficient to maintain the arc.

The lamp acts like a spark-gap in air, but with greater regularity. Pierce found that several discharges may occur during a single half-cycle of the transformer, the number increasing with decrease of capacity. Thus with 15,000 volts and a capacity of 0.117 microfarad he found that one or two discharges per half-cycle were obtained, while with a small capacity and the same voltage, over 200 complete discharges per half-cycle were obtained. The recovery is thus very rapid. The discharge of the condenser was never complete, the residual voltage being sometimes positive and sometimes negative. The resistance of the interrupter decreased with increasing capacity of the condenser and with decreasing inductance.

It was found during some experiments on the electric discharge through mercury vapour, that results somewhat similar to those described above were obtained. The

* Communicated by the Author.

† Proc. Amer. Acad. of Science, xxxix. (1904).

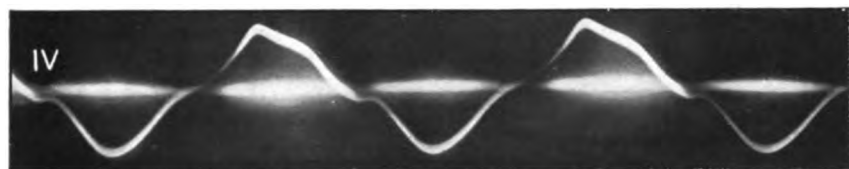
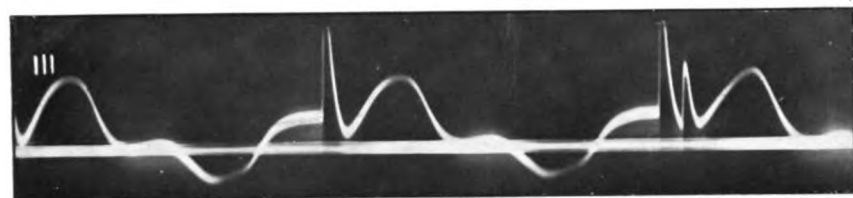
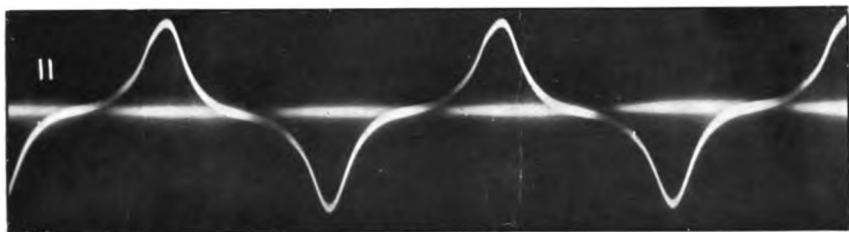
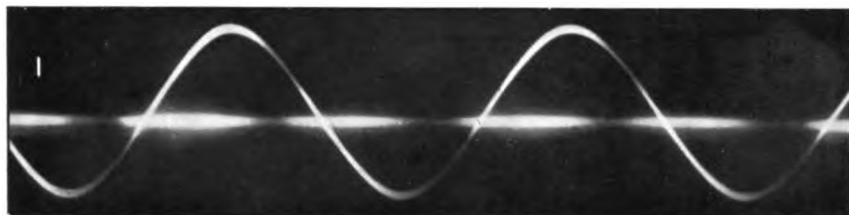
940 *Wave Form of Current through Mercury Vapour.*

discharge tube was a bulb about 12 cm. diameter, with two pools of mercury forming the electrodes ; the surface area of the two electrodes was different. The secondary of a transformer was connected to the electrodes, and an alternating current of period 60 per sec. and voltage 20,000 volts was sent through the discharge tube. A Duddell oscillograph was connected in series, and the current passing through the bulb was sufficient to cause a suitable deflexion of the vibrating mirror. The fibre in the oscillograph was so stretched that it was able to follow any variations in the current up to about 300 per sec.

When the discharge was passed without any self-induction or capacity in shunt with the tube, the wave form of the current was practically symmetrical and a sine curve. The addition of self-induction as a shunt caused each half-cycle of the discharge to become asymmetrical, *i. e.* the current increased at a slower rate, with an increasing voltage, than its rate of decrease after reaching its maximum value. The wave form was no longer a sine curve but became peaked at the maximum. The substitution of a capacity for the inductance in the shunt circuit altered completely the form of the discharge, as is well shown in Plate VII. (III.). With increasing voltage the condenser is charged and no current passes through the mercury vapour. At a certain critical voltage the condenser discharges with oscillations through the tube ; in the case shown two discharges were obtained, although owing to the applied voltage the condenser never completely discharged. This oscillatory discharge of the condenser only occurred during one half of the alternating voltage cycle. The wave form of the discharge during the succeeding half-cycle differed entirely and showed no oscillations. This asymmetry is due to the resistance of the discharge-tube depending on the direction of the current with electrodes of different surface areas. The amplitude of the current during one half-cycle was greater than that in the succeeding half-cycle.

Combining a suitable self-inductance with a capacity in shunt with the tube caused a unidirectional discharge of the condenser. This is illustrated in Plate VII. (IV.). In this case $\frac{R^2}{4}$ is greater than $\frac{L}{C}$. The discharge shows asymmetry in one half-cycle, and also the wave form depends on the direction of the current through the tube.

The oscillograms show that the addition of a capacity as a shunt to the electric discharge-tube increases the "peak" value of the current through the tube.



- I. No capacity or inductance in shunt.
- II. Inductance 0.42 henry in shunt.
- III. Capacity 0.09 microfarad in shunt.
- IV. Capacity 0.04 microfarad, inductance 0.62 henry in shunt.

XCIII. On the Critical Frequency of Pulsation of Tones. By
FRANK ALLEN, *Ph.D., Professor of Physics, University of
Manitoba, Winnipeg, Canada* *.

IN a recent communication with the above title to the *Philosophical Magazine* †, several relationships were deduced from the experimental data connecting D, the duration of a pulse of sound at the critical frequency of pulsation or flutter of a tone, P, the blowing pressure of the air in the tonvariator, to which the intensity of the sound is proportional, and N, the frequency of vibration of the tone.

The most important of these relationships is that connecting D and P, and was given in the paper:

$$D = K \sqrt{\log P + C},$$

where K and C are constants.

This equation, applied to the experimental measurements contained in Table II. in the former paper, gave a series of straight lines for different values of N, which were shown in fig. 3, p. 56, in the paper. The lines were so uniformly straight that it was concluded this equation completely satisfied the experimental data.

TABLE.

Pressure P.	log P.	D. N=170. sec.	D. N=180. sec.	D. N=200. sec.	D. N=240. sec.	D. N=264. sec.
2.40 cm.	.380	0.0203	0.0198	0.0189	0.0172	0.0164
2.20 "	.342	.0200	.0196	.0186	.0170	.0160
2.10 "	.322	.0197	.0192	.0183	.0166	.0157
1.98 "	.297	.0194	.0189	.0179	.0162	.0154
1.82 "	.260	.0191	.0186	.0176	.0160	.0151
1.70 "	.230	.0189	.0184	.0173	.0156	.0147
1.62 "	.209	.0186	.0181	.0171	.0153	.0144
1.53 "	.185	.0182	.0177	.0167	.0150	.0141
1.45 "	.161	.0177	.0172	.0162	.0143	.0124
1.25 "	.097	.0168	.0163	.0153	.0135	.0126

Reference was also made in the paper to the analogous

* Communicated by the Author.

† Vol. xlviii. p. 50 (1924).

equation of T. C. Porter, connecting D , the duration of a flash of light at the critical frequency of flicker, and L , the intensity of illumination of a black and white disk,

$$n = \frac{1}{D} = K \log L + C.$$

This equation, when applied to Porter's measurements on white light, was found to have two values for the constant, K , and therefore represented two straight lines with different inclinations, which met at a point representing the low illumination of 0.25 metre-candle.

As this peculiarity of Porter's law has been interpreted as applying to vision by the rods for dim light, and by the cones for bright, there seemed to be no reason why a similar phenomenon should occur in the perception of sound, since nothing suggestive of a double percipient mechanism corresponding to rods and cones exists in the ear.

The authors therefore felt satisfied that the square root of $\log P$ was involved in the sound measurements, and did not discover the direct relationship which is here shown to exist.

Recent unpublished work in the writer's laboratory on the sense of touch has brought to light a phenomenon of double action precisely similar to Porter's law in the visual sensation. In consequence of this discovery, the data on sound were re-examined in order to see if Porter's law held there within the range of intensities studied. On plotting the values of D , from Table II. referred to above, and $\log P$, each of the curves was found to consist of two straight lines similar to those found by Porter.

These are shown in the new figure in this paper. Each pair of lines represents observations made on a tone of the frequency indicated, when it was varied from the lowest to the highest available intensity. It may be remarked that Ives* found Porter's law to apply to each spectral colour with a suitable change in the constants. This was confirmed by the writer†.

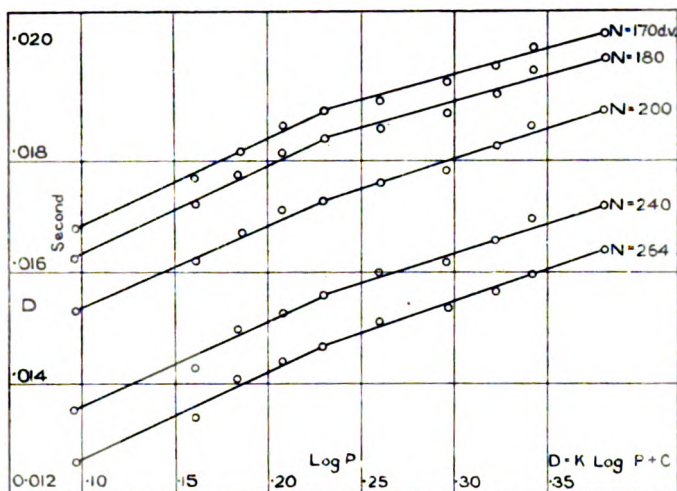
Table II. of the former paper is given here together with the values of $\log P$ instead of the square root of that quantity.

* Phil. Mag. vol. xxiv. p. 358 (1912).

† Phil. Mag. vol. xxxviii. p. 81 (1919).

The change in slope of the lines in the figure occurs in each case at an intensity given by the tonvariator when blown by an air-pressure of 1.70 cm. of water. This is a quite weak sound, and is comparable with the position of the analogous point found by Porter at the intensity of 0.25 metre-candle.

In the former paper it was pointed out that Porter's law requires the reciprocal of D , whereas in sound D appears directly.



Porter found the angle of inclination made by the upper line representing high intensities to be nearly twice that of the lower. Inserting the numerical values of the constants, Porter's law may be written

$$n = 12.4 \log L + 10, \text{ for high intensities,}$$

and

$$n = 1.56 \log L + 17.75, \text{ for low intensities.}$$

The lower branches of the curves for sound in the figure are practically parallel, with a mean angle of inclination of $24^\circ 52'$. The upper branches, for more intense sounds, slightly converge, that for $N = 170$ d.v. having an angle of 15° and the others successively, 16° , $17^\circ 30'$, $17^\circ 45'$, and $18^\circ 30'$. In the analogous case of colours Ives found a similar convergence of the lines.

Porter's equations applied to sound may be written

$$D = 0.01558 \log P + C, \text{ for low intensities}$$

and

$$D = 0.01027 \log P + C, \text{ for high intensities,}$$

where 0.01027 is the mean value of the five constants, which range from 0.00932 to 0.01134.

The values of C vary for the different curves, and apparently are not physiologically significant, unless possibly they may have some connexion with threshold values. It will be noticed also that the larger value of the constant, K , in Porter's equations is for high intensities, whereas the opposite is the case with sounds.

Since Porter's law is derived from Fechner's law*, which is fundamental in sensory nerve action, it ought, therefore, to follow that the fundamental sensory actions and reactions should be similar with all the sense organs. The peculiar alteration of direction of the lines when changing from weak light to strong ought also to be found when changing from any weak sensory impressions to strong. This we now find to be the case with the sensations of sound and touch in addition to that of light.

In light, the Porter effect, as we may conveniently term it, has been referred to the change from rod vision to cone, and therefore has been regarded as confirmatory of the Duplicity Theory of Vision of von Kries. But from the additional evidence adduced here, such an interpretation becomes extremely improbable. The Porter effect appears to be a general property of the sensory nervous system, and hence must be referred to some fundamental property that all such nerves possess in common. The most probable location of the effect appears to the writer to be in the synapses, which Sherrington has found to possess a large number of important functions in nerve conduction.

As it is the intention of the writer to discuss this subject more fully when the experimental data now accumulating are complete, only this addition to, and correction of, the former paper, and its most obvious implications, are noted at present.

On p. 56 of the paper referred to the value .0311 in Table II. should be .311, and on p. 57 the word "arbitrary" should be omitted from the last line, as the constants are determined by the nature of the phenomenon and by the mode of experimentation.

* Peddie, 'Colour Vision,' p. 162.

XCIV. *The Non-Metallic Elements. Connections between their Dielectric and other Physical Properties.* By G. L. ADDENBROOKE*.

BOLTZMANN, in 1873, described a method of obtaining dielectric constants by observation of the attraction of a small sphere of a dielectric hung near a large charged sphere, as compared with the attraction of a similar small metal sphere taken as a standard.

There is a full description of this work, with a memoir specially written by Boltzmann himself, in Gordon's 'Electricity and Magnetism.' See also Poynting and Thomson's 'Electricity and Magnetism,' 1914.

The pulls found were connected with Dielectric Constants (K) by the equation :

$$\frac{\text{Pull on dielectric sphere}}{\text{Pull on metal sphere}} = \frac{K-1}{K+2}.$$

It is noteworthy that Boltzmann arrived at this relation by purely electrical reasoning, the steps of which are given by Gordon.

Boltzmann first found the dielectric constants of four different substances by putting plates of them between two electrodes.

He then found their dielectric constants by his attraction method and showed that the results were practically identical. The work was afterwards extended by his pupils over a wider range of dielectrics. Boltzmann's formula thus shows the connexion between two quantities, each of which can be measured directly and separately.

In the limiting case of a parallel or symmetrical field, the two electrical opposite pulls on the dielectric are equal, and therefore there is no movement of the dielectric as a whole; but taking two vertical plates as electrodes, Thornton (Proc. Royal Soc. A, vol. lxxxii., 1905) hung a thin ellipsoid of a dielectric centrally between them and thus in a symmetrical field, the long axis perpendicular to the plates. On charging the two plates oppositely there is no movement, but if the ellipsoid is slightly rotated axially by momentarily twisting the suspension, its period of oscillation is longer when there is no electric field than when the field is charged. Thornton showed by a large number of experiments that, from the difference in time of the swings, dielectric constants can be obtained agreeing with those found by ordinary methods.

* Communicated by the Author.

Phil. Mag. Ser. 6. Vol. 47. No. 281. May 1924.

3 P

In Boltzmann's arrangement the dielectric is bodily drawn towards the stronger field. In Thornton's, where the field is symmetrical, if the ellipsoid is rotated, the lines of force running partly through it are lengthened, and the two opposite pulls produce a restoring torque owing to the lines of force tending to shorten themselves.

While, for longitudinal movement of the dielectric, divergence or want of symmetry of the field is thus necessary, it is interesting and important to note what a small divergence is needed to get a substantial pull.

In the description of Boltzmann's work mentioned above, all the data and dimensions used are given. Assuming that the divergent field radiates from the centre of the charged sphere, the solid angle subtended between this point and a vertical section through the centre of the attracted dielectric sphere was under 10° . Again, I have set up a working model of Boltzmann's arrangements, but using a fine metallic strip suspension instead of his bifilar suspension with the threads at a considerable angle. Working on modern lines, it is clear that far greater sensitiveness can be obtained, and that, with potentials on the inducing sphere such as Boltzmann used, readable deflexions could be obtained at several times the distance at which he worked, and thus the angle of divergence of the field could be reduced to 2° or 3° . The extension of Boltzmann's reasoning to symmetrical fields where the two opposite pulls equalize each other is therefore a short step.

Converse Use of Boltzmann's Formula.

Consequently, if we know the value of K for a dielectric, as found by any recognized method, by placing this value in the above equation we can get the relative attraction of a sphere of a dielectric placed in a standard electric field, the attraction of an equivalent metal sphere being taken as unity.

The substantial nature of these attractions does not seem to be generally recognized.

For instance, in the Phil. Mag. for March 1923 there was a communication by me on the "Properties of a Flint Glass of Density 6," which had a dielectric constant of 13.

Taking the attraction on an equivalent metal sphere as unity, we get for the attraction in this case :

$$\frac{\text{Pull on dielectric}}{1} = \frac{13-1}{13+2} = \frac{12}{15} = .8;$$

that is, the pull on a sphere of this dielectric in an electric

field would be eight-tenths of that on a metal sphere of the same size. Similarly the pull on a sulphur sphere of $K=4$ is $\cdot 5$, and that on a paraffin sphere of about $K=2$ is $\cdot 25$. These facts are worthy of the serious attention of physicists studying the now accepted view of the nature of the atom.

Consideration of the Two Actions taking place when a Dielectric is placed in an Electric Field.

Consequently, when a dielectric is placed in an electric field and the potential difference is maintained constant from an outside source there are two measurable actions:—

- (1) Ordinary capacity, or the electric storage action, the energy stored corresponding to $\frac{1}{2}QV$, or the quantity stored multiplied by half the potential difference.
- (2) The actual pull on the dielectric, as explained above.

If a condenser with nothing between the plates except the æther is charged, a certain storage of energy takes place. If, then, a dielectric is inserted there is an additional storage of energy. The initial charge plus this additional charge divided by the initial charge is called the "dielectric constant," usually denoted by K . The question then is: Does the original storage of energy in the field disappear after the dielectric is inserted and become part of the energy stored in the molecules of the dielectric, or does it still exist as a separate entity? (See Drude's 'Optics,' p. 387.)

The modern view of the atom has now obtained general assent. A dielectric, therefore, consists of minute opposite point charges occupying a nominal space in the included æther, and the view is strengthened that, when a dielectric is inserted in an electric field—if the potential slope is maintained from an outside source—the storage of energy between the boundaries of the field is not appreciably altered, but that there is an additional and separate storage in the action which arises between the charges of the nuclei and electrons of the atoms of the dielectric and those of the electrodes which give rise to the field.

In a communication to the Phil. Mag. for March 1922, on a "Study of Franklin's Experiment on the Leyden Jar," I showed that, contrary to what is often taught, the action of an electric field on a dielectric is purely inductive, and that the charge disappears entirely when the field is removed, apart from any absorption. Absorption with good

dielectrics is small or negligible, in comparison with the instantaneous charge, for charges at ordinary alternating frequencies, though it may be a large factor if the time of charge is relatively long. Absorption can, however, be distinguished from instantaneous charge, as it is always accompanied by losses of corresponding magnitude, which can be separately measured with alternating fields by the electrostatic wattmeter and otherwise (see above communication, *Phil. Mag.* March 1923).

In this paper, therefore, the value of the additional action corresponding to $(K-1)$ is alone taken as a basis for comparing the relative amounts of energy stored by different dielectrics in given electric fields, and also for comparisons of the energy stored with the corresponding attractions; it will be called the "reversible energy storage equivalent," or "dielectric equivalent," a quantity which is less abstract than the term "dielectric constant."

Looking at Boltzmann's formula, it will be seen that it is also based on $(K-1)$ and not K .

There are, therefore, two separate actions which we can measure by putting dielectrics in electric fields:

- (1) The additional reversible energy storage corresponding to $(K-1)$;
- (2) The attraction, pull or stress measured directly and corresponding to

$$\frac{K-1}{(K-1)+3} \quad \text{or} \quad \frac{K-1}{K+2}.$$

Relation of Attraction to Energy Reversibly Stored.

If a series of values of energy reversibly stored is plotted in a diagram corresponding to different values of K , or $(K-1)$, a rising straight line is obviously obtained.

If the corresponding attractions for the same range of values of K are plotted, the result is a curve.

Consequently, if relative values of energy reversibly stored and the corresponding attractions are compared over more than short ranges, considerable differences appear, as will be shown more fully later.

It therefore seemed desirable to have separate data for these attractions, also that comparisons of electric with other physical actions should not be based solely on K , or the energy stored in the dielectric plus that stored in the field, as is usually the case now, or even on $(K-1)$ alone.

Necessity of Using Atomic Values for Comparisons.

Since Faraday's time, however, it has been accepted that the action of an electric field on dielectrics is on their molecules. To make proper comparisons of the molecular attractions, or of their corresponding dielectric equivalents ($K_m - 1$), or reversible energy storage values, measurements must therefore be made of both actions on the same number of molecules in all cases.

Method of Obtaining Molecular Values of $K - 1$.

To obtain the molecular dielectric equivalents, or ($K_m - 1$) of dielectrics, we can proceed as follows:—

The number of molecules in a standard volume of any dielectric is proportional to the atomic volume of the substance, *i. e.*,

$$\frac{\text{Atomic weight}}{\text{Density}} = \text{Atomic volume.}$$

If, then, we write

$$(K - 1) \times \frac{AW}{D} = K_m - 1,$$

we get numbers which are proportionate to the values of the energy reversibly stored molecularly in different dielectrics, the procedure being similar to one which is frequently used by optical workers substituting N or N^2 for K .

But, while this is sufficient for getting a set of relative values of ($K_m - 1$) or of the energy reversibly stored, to get the relative molecular attractions we must have not relative, but actual, magnitudes for K_m . These values could be found experimentally if spheres were taken, the respective volumes of which were proportionate to the atomic volumes of the substances. We should then get spheres of different sizes and weights, the attractions of which would have to be compared with the attraction of a standard metal sphere. The same results could also be obtained by measuring the capacities of dielectrics between flat plates a standard distance apart, but varying the area of the plates to correspond with the atomic volume of the different dielectrics. The values can, however, be obtained with close approximation by calculation.

Application to Data for Elements.

What has been said above is of a general character, and is applicable to dielectrics of whatever nature. In this communication it is proposed to apply the conclusions

reached only to a study of the electric properties of certain elements.

The dielectric constants are now available for ten elements, including liquefied elementary gases, and investigations by the writer on absorption in dielectrics lead to the conclusion that the accepted dielectric constants of these elements (see Table I.), taken from the 1913 Tables of the French Physical Society, although not free from small observational errors and small differences due to absorption, are, nevertheless, sufficiently accurate to form a fair basis for considering the dielectric properties of these elements.

TABLE I.
Properties of Non-metallic Elements.

Element.	Atomic Weight.	Density.	$\frac{AW}{D} =$ Atomic Vol.	K. Dielectric Constant.
Hydrogen, Liquid	1	·071	14·1	1·21
Nitrogen, Liquid	14	·88	16	1·45
Oxygen, Liquid	16	1·25	12·8	1·47
Chlorine, Liquid	35·5	1·5	23·6	1·97
Bromine, Liquid	80	3·2	25	3·10
Iodine, Solid	127	4·66	27	4·00
Phosphorus	31	1·84	16·8	3·85
Sulphur	32	2·0	16	4·00
Selenium	79	4·28	18·3	6·14
Carbon	12	3·5	3·4	5·5

By referring to the above list, it will be seen that the atomic volumes of the three halogens are the largest, and also that they are nearly equal and cover an important and considerable range of the attraction curve. If, then, we make the atomic volume of one of them, say chlorine A.V. 23·6, our standard, the $(K_m - 1)$, or molecular $(K - 1)$, will be the same as that of the element in its natural (liquid) state, and this will also be nearly true for the other two halogens, bromine and iodine, which will therefore come in their right places.

If, then, we divide the relative values for all the elements by the atomic volume of chlorine, we shall get closely correct values of the corresponding molecular dielectric equivalents, or $(K_m - 1)$, and correct magnitudes for subsequent insertion in Boltzmann's formula, $\frac{K_m - 1}{K_m + 2}$ as used for finding the relative attractions.

The molecular values for $(K_m - 1)$ are given in Table II., column 2.

TABLE II.

Molecular Dielectric Equivalents of Elements, Actual and Comparative, on the Basis of the Natural Number of Molecules in Chlorine.

Element.	2. Actual Values of $K_m - 1$, or Energy stored.	3. Relative Values of $K - 1$, or Energy stored.	4. Relative Values, $K_m - 1$ $K_m + 2$ Attractions.
Hydrogen	·126	1·0	1·0
Nitrogen	·30	2·4	2·27
Oxygen	·256	2·02	1·98
Carbon	·65	5·2	4·5
Chlorine	·97	7·7	6·1
Bromine	2·22	17·8	10·5
Iodine	3·4	27·7	13·3
Phosphorus	2·0	16·2	10·0
Sulphur	2·04	16·2	10·1
Selenium	4·28	32·2	14·25

Inspection shows that the lowest value of $(K_m - 1)$ thus obtained is that for liquid hydrogen. Taking this as unity, all the other values are divided by it. We thus get a table of the comparative values of the energy reversibly stored in an electric field of standard potential slope for the elements here considered (see column 3, Table II.).

The corresponding relative values of the molecular electric attractions are given in column 4 of Table II. These are found by taking the values in column 1 and placing them in the equation $\frac{K-1}{K+2}$, and then taking the value found for hydrogen as unity.

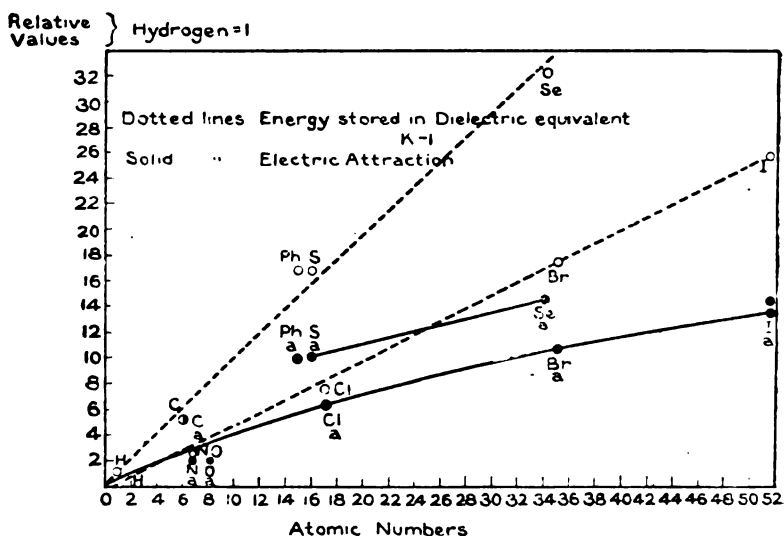
If, now, these two lists are compared, it will be seen that while the values in both increase nearly equally for the lower values of K , they diverge when the values become higher, and, finally, for $K=6$ (the largest value obtained for an element so far) the relative value of the energy storage is more than twice the value of the corresponding attraction.

Deduction from Curves based on the Data in Table II.

Before proceeding further, it will be useful to plot the above results as curves with Columns 2 and 3 of Table II. as ordinates, and as abscissæ Atomic Weights or Numbers. Curves for both sets of properties do not essentially differ, but on the whole the relations appear a little more direct for Atomic Number than Weight, and therefore the curves below are worked out on this basis. Anyone, however, with the data can easily draw similar curves with abscissæ representing Atomic Weight.

Fig. 1.

Relation of Energy stored, and Attraction, to Atomic Number.



The intimate connexion between Atomic Weight and Number and the atomic ($K-1$) or dielectric equivalents of elements is manifest for the two groups Sulphur, Phosphorus, and Selenium, and secondly, Chlorine, Bromine, and Iodine, and also the corresponding relation with Atomic Attraction. These two sets of elements belong to well-defined and separate groups in the Periodic Table. Consequently, the connexion of the dielectric properties of these six elements with Atomic Weight, Number, and Position in the Periodic Table is well defined.

As regards the other four elements plotted, they each belong to separate groups in the Periodic Table, and data for further elements in these groups are so far wanting. The

evidence of the first six elements, however, permits a fair inference that the dielectric properties of these four elements also must probably be related in a similar way to Atomic Weight, Number, and Position in the Periodic Table. Further evidence that such is the case can be obtained by study of the optical properties of the dielectric elements on the above lines, as the optical data for a larger number of elements are known.

Further inferences can be drawn from study of this and other somewhat similar diagrams. Enough for the present purpose, however, has been said here in drawing attention to the fact that the electric properties of the elements are in the first place closely related to their Atomic Numbers and Weights, and in the second to their position in the Periodic Table. Their ordinary dielectric properties are, therefore, related to their chemical and physical properties in a very fundamental manner. The point is further made manifest that though the curves for energy stored and for attraction both show equal regularity, as the atomic weight or number gets higher, the relative amount of electric energy atomically stored in an electric field increases progressively as compared with the values of the corresponding attractions.

The curves also support Faraday's original view that the action of electric fields on dielectrics is directly on their atoms or molecules.

Note 1.—Experience shows that the dielectric constants or equivalents of the elements, when free from absorption, have very small temperature coefficients like the refractive index. In all the elements dealt with here, Maxwell's law is obeyed fairly closely, that $K=N^2$, the square of the refractive index.

Note 2.—The above procedure is very similar to that used for obtaining atomic or molecular refractivities, from N^2-1 , this being the Lorentz formula. Optical workers always, however, write :

$$\frac{N^2-1}{N^2+2} \times \frac{AW}{D} = \text{Atomic Refractivity.}$$

The procedure above is rather different. Instead of making the correction in one operation, the molecular value of $K-1$, or N^2-1 is first found from $(K-1) \frac{AW}{D}$, and the figure thus obtained is afterwards inserted in the Boltzmann or Lorentz equation.

For the small values or variations of N usually discussed in optical work, there is little difference between the results given by the two formulæ, but over such ranges as those above the difference may be as much as 16 per cent. It is submitted that the method adopted above is physically correct, and should be used for optical wave-lengths also.

Note 3.—In the above tables it has been necessary to take the dielectric constant of liquid hydrogen from the square of the refractive index. The dielectric constant of hydrogen gas agrees almost absolutely with N^2 . For oxygen and nitrogen both the gaseous and liquid dielectric constants agree closely with N^2 . There are also other reasons which lead to the conclusion that the dielectric constant of liquid hydrogen of the density taken above is 121. The risk in assuming this value seems almost *nil*. Again, if it were incorrect the general conclusions arrived at would only be slightly affected.

It would appear that with modern methods of electric measurement and the means there are now of producing large quantities of liquid hydrogen, it should not be impossible to get the dielectric constant directly.

*Comparisons of the Relative Electric Values found with the
Relative Values of other Physical Properties.*

General Observations.

If dielectrics are taken at zero temperature (absolute), their molecules are not subject to the alternate attractions and repulsions of the electromagnetic waves of heat passing over them, and no heat is stored in the substance. Again, the molecules are in the closest proximity to each other, and any attractions between them are of the maximum strength.

Suppose these molecules, while at rest, are subjected to the action of heat waves which are also electromagnetic waves or pulses of gradually increasing intensity. They will be acted on by the waves and will also be alternately attracted and repelled as the waves pass over them. Thus they will be thrown into a state of vibration of gradually increasing amplitude. That is, the heat waves will introduce forces which, on the whole, oppose the natural attraction of the molecules for each other. As to this, Nernst, in his 'Theory of the Solid State,' says:—

“*Melting Point.*—Lindemann introduced the hypothesis that the melting point is determined by the fact that at this temperature the amplitude of the vibrations of the atoms round their positions of rest becomes commensurable with the atomic distances.”

If this is so, when the vibrations reach this amplitude the electric lines of force uniting the atoms or molecules can no longer be constantly directed to one set of neighbouring atoms, but they will equally be directed momentarily to others; consequently the force of cohesion, if this is electrical, will be largely nullified, and the tendency of the natural attractions to keep the substance in a definite formation will be overcome. Thus a considerable change of state will occur.

It seemed that, if there were substantial ground for this belief, some signs of connexion might be found between the relative absolute melting-points and the relative values either of the molecular energy stored in an electric field, or of the corresponding attractions, and comparison was made on the following lines.

Comparison of Electric Actions with Absolute Melting-Points.

Taking the absolute zero of temperature as basis, the relative values of the melting-points of the elements above this were found. Next, the melting-point of liquid hydrogen being definitely abnormal (a matter which will be referred to again later), that of liquid oxygen was taken as the standard and called 2, to agree with the relative values of both electrical actions. The relative values of the melting-point for the other elements were then divided by half the value for oxygen. The final set of proportional values thus found is given in Table III., column 4, where it can be compared with the relative values of the electrical energy reversibly stored (column 2), and, again, with the corresponding attractions (column 3).

TABLE III.
Relative Values of Different Physical Properties.

Elements.	Electric.		Thermal.	
	Energy stored.	Attractions.	Melting Points.	Boiling Points.
Hydrogen	1.0	1.0	0.5	0.5
Nitrogen	2.4	2.27	2.3	2.33
Oxygen	2.0	1.98	2.0	2.00
Carbon	5.2	4.5	—	—
Chlorine	7.7	6.1	5.4	6.0
Bromine	17.8	10.5*	8.4	8.4
Iodine	27.7	13.3	12.2	11.4
Phosphorus	16.2	10.0	10.0	9.0
Sulphur	16.2	10.1	12.2	17.9*
Selenium	32.2	14.3	15.6	24.0*

* See observations below.

The connexion between the relative melting-points and both electrical actions is evident, but is much more direct over the whole range for the attractions than for energy stored. In fact, the corresponding relative values of the attractions to the melting-points are so close in some cases that they approach coincidences. There is also reason to believe that if the fundamental electrical data were more accurately determined the correspondences might be still clearer.

It is hardly possible that there should be such a series of correspondences over such a range unless an intimate fundamental connexion underlay both physical actions.

The connexion predicated is, from the nature of all the actions, electric attraction. If this is accepted, it then seems to follow that the attraction of an outside electrical field for the molecules of a dielectric must actually be a fairly close proportional measure of the attractions of the molecules themselves for each other. This implication is further emphasized if, in addition to comparisons with melting-points, we next make them with the corresponding boiling-points.

Comparison with Absolute Boiling-Points.

Proceeding in the same way as with the melting-points, a table of the relative values of these was got out, using the absolute zero as a basis as before. The relative values of the boiling-points are given in Table III., column 5. With two exceptions, the coincidences are again practically as close as with the melting-points. As regards the differences, and one or two other points in the two tables, the following observations may be made.

The values for hydrogen come to about half the values for the corresponding dielectric equivalents, and in the boiling-point table the values for sulphur and selenium are about 50 per cent. too high. The first of these differences may be connected with the change in the specific heat of hydrogen between the liquid and gaseous state. In the second case, Ramsay points out in his 'Chemistry' that, at the temperature necessary to bring sulphur and selenium to the boiling-point, there is preliminary molecular dissociation in addition to simple change of state, thus raising the boiling-point. It is proposed to defer further discussion of these and some other matters until later.

Again, recent experimental work on bromine leads to the view that the accepted dielectric constant is rather high. Further experiments are in progress to test this, for which

Professor H. B. Baker has kindly supplied his highly dried bromine. It is hoped to report the results later.

As regards the importance of the melting and boiling points in arriving at a more complete knowledge of the constitution of matter, two further passages from Nernst's work already mentioned may be quoted.

"An especially simple significance attaches to the work which must be expended to break up a solid body into its constituent molecules, and to separate these molecules to definite distances from one another. *The latter occurs when a solid body is sublimed.*

"For crystalline substances—and we shall always (unless otherwise stated) picture to ourselves a solid body as a crystal, since the amorphous state is known to be a continuous transition of the liquid state of aggregation—the melting point is a specially characteristic magnitude."

Relation of Relative Molecular Electric Actions to Heat of Vaporization.

The question next arose whether the correspondences so far found would still persist for the relative heats of vaporization. The data I have been able to find only extend to six elements, and one of these, viz. iodine, has to be melted at a considerably higher temperature than the others before being vaporized. The heat necessary to change iodine from a solid to a liquid is, however, available and has been added in this case. The conditions generally do not allow of comparison to a close percentage of accuracy, but the relative values come out as follows:—

TABLE IV.

Relative Molecular Amounts of Heat Absorbed in Change from Liquid or Solid State to Vapour.

Elements.	Relative Values of Vaporization.	Molecular Attractions.
1.	2.	3.
Hydrogen.....	·5	1·0
Nitrogen	1·8	2·3
Oxygen	2·0	2·0
Chlorine	5·4	6·1
Bromine	9·5	10·5
Iodine	12·0	13·3

In this case, though the agreement is ostensibly with the corresponding relative attractions, relative heats of

vaporization should be more naturally comparable with relative amounts of energy reversibly stored or $(K_m - 1)$. As regards this, it will be seen from Table II. that the relative values for energy stored, or $(K_m - 1)$, and for the attractions have practically the same ratios for the three elementary gases in liquid form. Investigation shows that they have also the same ratios in the gaseous form. As regards liquid chlorine and the other elements where differences begin to appear, there is further evidence which seems to lead to the view that the relative values of the energy reversibly stored $(K - 1)$ and of the corresponding attractions preserve a fairly constant ratio from element to element when these elements are in the state of gas or vapour; the relative increases in energy stored arise in the liquid and solid states or as aggregation increases. This point will be referred to again later.

Further Considerations.

Trouton's rule states that, with certain remarkable exceptions (viz. helium and hydrogen),

$$\frac{\text{Heat of vaporization}}{\text{Boiling temp. (abs.)}} = \text{constant.}$$

Now we have seen above that the relative values of both these quantities agree with the relative values of the corresponding electric attractions for different elements. We can therefore apparently re-write Trouton's rule and say:

$$\frac{\text{Electric attraction overcome in vaporization}}{\text{Electric attraction overcome at boiling-point}} = \text{constant,}$$

remembering that the attraction in vaporization is also proportional to energy stored.

Again, it is pointed out in such works as Nernst's 'Theoretical Chemistry' that if the absolute melting-points of substances are taken as 2 in each case, the absolute boiling-points have approximately relative values of 3, and the critical temperatures of 4, and the connexion between them and the heat of vaporization is given by Trouton's rule. Consequently, the electric attractions, as shown above, are intimately connected with, and must be more or less proportional to, the values of all these properties, including the critical temperature in each of the elements we are dealing with.

But the relation of the boiling-points to the values of

osmotic pressure is further well recognized, and osmotic pressures can be found by the lowering of the freezing-point or the raising of the boiling-point in the case of Solutes. Consequently it seems to follow that there are also intimate relations between the electric attractions and osmotic pressure in addition to the connexions shown above.

It is impossible here to go into all these actions in detail, but as it is already recognized that all this group of fundamental interactions between heat and matter are interconnected, if what has been said above is in principle correct, the basis of the connexion is evidently the electric attraction of the molecules of different substances for each other, and this attraction can be found in the case of dielectrics by the method worked out by Boltzmann in 1873, when extended as above.

The above results further seem to show that the atomic or molecular electric attractions involved are of the usual character and obey the ordinary electric laws.

Relations of Energy Reversibly Stored in Electric Actions to the Energy Stored in Heat Actions.

Though in dielectrics the primary connexion has been shown to be with electric attraction and not with energy stored, nevertheless electric attraction and the electric energy stored in dielectrics in electric fields are closely related, since we can measure them both, and by Boltzmann's formula can derive one from the other. The question then arises why the relation is so direct for the attraction while the energy stored under the same conditions shows increasing differences from the corresponding attractions as we progress from liquids at very low temperatures to liquids at ordinary temperatures, and still more markedly to solids.

The answer, apparently, is that when we measure the capacity of a dielectric we are measuring the energy reversibly stored in it in several different ways:—

- (1) Between the boundaries of the field.
- (2) In polarizing internally the individual atoms and molecules or changing them into doublets, and thus altering their attraction for each other also.
- (3) In displacing the atoms or molecules bodily and setting them into vibration.
- (4) In effecting smaller concurrent changes.

The reason why hitherto so little correspondence has been found between the values of the dielectric constant of substances and other physical actions is evidently because we must know something of the relative values of the energy involved in the above different actions separately before clear and quantitative connexions can be established.

If we turn to the phenomena of heat, it has for a long time been accepted that, when a substance is put in an alternating field of the frequency of heat waves, the energy impressed, in the case of solids, is stored in different ways, of which two account for the greater part in more or less equal proportions (see Nernst's 'Physical Chemistry,' 1913, p. 260).

It seems probable that as heat energy is stored in a dielectric in these different ways, the same, or nearly so, may be the case when dielectrics are placed in ordinary electric fields, and that more energy may be stored for a given stress in some cases than others.

Now if the lists of the relative values of the attractions and energy stored (Table II.) are examined, it will be found that there are differences between the relative values of the attractions and energy stored in the case of the solids of the order of those suggested by thermodynamic theory, the differences falling off from solid to liquid and liquid to gas.

I do not put forward this as more than suggestive at the present stage, but further experiments are practicable which would throw a much clearer light on this part of the subject.

Relations of Electrical to Mechanical Attraction.

The above comparisons have been made between the actions of ordinary electric fields on matter and those of heat. It is possible, however, to make comparisons of a more direct nature, in which the electric attraction is compared directly with mechanical forces or pulls.

Relations with Surface Tension.

The cohesion of different kinds of elementary matter must be allied more or less directly with the corresponding surface tension. Unfortunately the surface tensions of only a few of the elements we are dealing with are available, and have necessarily been obtained under somewhat different conditions; but the relative molecular values show an unmistakable connexion with the corresponding values for the electric attractions.

The data in the Table below were kindly corrected by Mr. Hatschek. He also raised the point of the basis on which calculations should be made. They have been made on the assumption that the active atoms are a single surface layer. The numbers of atoms in a given length will therefore be inversely proportional to their diameters. These have been calculated from the atomic volumes given above.

The columns in the table below show :—

1. Observed superficial tension in dynes per cm. The letters indicate the temperatures. B, near boiling point, F, fusion point ; in two cases the temperatures are given.
2. Relative Superficial Tensions taking Oxygen (2) as basis.
3. Relative atomic diameters taking that of Oxygen as unity.
4. Relative atomic tension (Col. 2) $\times$ (Col. 3).
5. Corresponding relative atomic electric attractions.

TABLE V.

Element.	Surface Tension Actual.	Surface Tension Relative.	Atomic Diameter Relative.	Surface Tensions Atomic.	Electr. Attrac. Atomic.
Oxygen	13.0 B	2.0	1.00	2.0	2.0
Chlorine.....	33 - 72°	5.2	1.23	6.4	6.2
Bromine.....	62 + 21°	9.4	1.25	11.7	10.0
Phosphorus	41.0 F	6.2	1.1	6.8	10.0
Sulphur.....	42.0 F	6.2	1.2	7.4	10.0
Selenium	70.0 F	10.7	1.15	12.3	14.25

The results can only be a first approximation, but they seem definite enough to show an intimate relation with electric attraction which would probably be closer could proper corrections be applied. The greatest differences are with phosphorus and sulphur which behave rather indefinitely about the melting point.

These results connect the electric properties directly with the forces of cohesion. It must be remembered, however, that the actual forces in cohesion as found in solids in the mass are also dependent on molecular aggregation and crystallization. The forces of cohesion between a mass of crystals may differ widely from the forces within a single crystal.

Surface Tension has already been connected with latent heat : see 'Surface Tension and Surface Energy,' Willows and Hatschek, p. 11. Consequently there is a connexion between latent heat and the electrical properties also.

Comparison with Capillarity.

Here again we can compare the electrical pull with the mechanical, but with the interesting difference that the atoms are separate and much more in the same state as in the gaseous condition.

When liquids are brought into contact with the surface of solids, attraction usually takes place.

Early work showed that small percentages of salts in the water usually increased this attraction in different degrees. The salt in such solutions is ionized and exists in the form of oppositely charged ions, only one kind of which will be attracted by the glass, namely, that having the opposite charge to the glass.

By a large number of comparative experiments on salts of varying composition, Schiff (see Smiles's 'Chemical Constitution and Some Physical Properties,' p. 34) arrived at an estimate of the relative attraction values of the separate ions in the case of six of the elements we are dealing with. These comparative values are given in Table VI. in terms of hydrogen. They agree substantially with the relative values of the dielectric attractions. There are similar relations, though not numerically so close, with viscosity.

TABLE VI.

Elements.	Capillarity.	
	Relative Tensions:	Relative Molecular Attractions.
Hydrogen	1	1
Nitrogen	2—3	2.4
Oxygen	2—3	2.0
Chlorine	6—7	5.9
Bromine	11—13	10.5
Iodine	19*	13.3

* With iodine there is apparently dissociation.

There are certain margins in these correspondences, due no doubt to the difficulty of exact experiment, and also to the fact that some dissociation must have taken place in one or two cases ; for instance, in the case of iodine.

The correspondences, however, are sufficiently close to predicate an intimate connexion between the attraction of the separate ions of an element for the glass used as a standard of attraction and the corresponding attractions of an electric field for the same ions aggregated together in an ordinary state. The results show that the character of this natural attractive force is apparently only fractionally altered when the molecules are aggregated, as compared with what it is when they exist separately in a solution.

Finally, it is to be observed that, while water with different salt solutes has been used as above for finding variations in capillary attractions, the solutions are essentially electrolytic, and similar to those used by Gladstone and Dale for obtaining specific refractivities.

Maxwell's Relation and the Relations of Electric Energy Stored and the Corresponding Attractions to Optical Phenomena.

In addition to the correspondences found above, there are similar, and in some cases even closer, relations with the so-called "optical properties."

In all that has been said so far, reference to the optical relations has been avoided in order to establish the results from the purely electrical standpoint.

Maxwell's relation that K should equal N^2 is, however, verified—at least the two quantities are closely of the same order—for all the elements dealt with here, and there is evidence that the same is also most probably the case for the rest of the nineteen dielectric elements, or at any rate for sixteen of them.

Consequently, with fair approximation, we have for all the above elements :

$$K_m - 1 = N_m^2 - 1 \quad \text{and} \quad \frac{K_m - 1}{K_m + 2} = \frac{N_m^2 - 1}{N_m^2 + 2},$$

the latter being the Lorentz formula. As used in optics, the two formulæ have had a theoretical basis, but as for long waves they are associated directly with energy stored and with attraction respectively, it seems a fair inference that they must be similarly associated with the similar actions occurring at the frequencies of light and heat.

Since in both cases we start with fair coincidence, if two lists of relative values for $N_m^2 - 1$ and $\frac{N_m^2 - 1}{N_m^2 + 2}$ are made on the same lines as above, the figures obtained

for all the elements will correspond, except for fractional differences, with those already found above on a purely electrical basis.

Conclusion.

In the case of surface tension and capillarity, a static or gravitational pull is balanced against the steady electric attraction of the molecules for each other or for a standard. In the melting and boiling points, the disruptive or shaking action of the electric waves is balanced against the steady natural electric attraction between the molecules. Thirdly, in vaporization the connexion seems to be with the energy stored, which is also proportionate to the attraction. Finally, heat and light waves so overlap in frequency that what is true for the one must almost certainly follow (speaking generally) for the other.

The difference between the effects of long electric waves and short in dielectrics seems chiefly to lie in the fact that with long waves we have a single potential slope throughout the dielectric, while with light and heat waves there are nearly always a number of complete waves in its thickness. Consequently, some of the molecular condensers subjected to light and heat waves are receiving a charge at the same time that others are discharging. This causes important differences, but rather of detail than of principle, and chiefly in the initial application and dying down of the field.

Thus, as outlined above, the electric attraction and the phenomena of capacity in dielectrics can be brought into line, speaking generally, with work which has been done optically or at light frequencies, and both are brought into close relation with the phenomena of heat, surface tension (which is closely allied with cohesion), and capillarity.

Space here only permits of allusion to the further connexions which exist between the electrical properties of these elements as defined above and their atomic weight or number, position in the Periodic Table, and chemical action. It is hoped to discuss these later.

The substances dealt with above include the two elements (hydrogen and oxygen) from which water is formed, and also the four elements (hydrogen, oxygen, nitrogen, and carbon) which are the basis of all organic compounds. If chlorine, sulphur, and phosphorus are added to these we have also the main constituents (apart from calcium, silicon, and sodium) of all animal and vegetable life. They also include the elements composing most of the dielectrics used in science and engineering.

The importance of obtaining the electrical properties of these dielectric elements exactly, and of connecting them with other physical properties, is thus obvious. Again, these elements form a number of compounds between themselves, the electrical properties of which can also be measured, and thus a sound basis can be established for finding the electrical effects of chemical combination.

Having got as far as has been shown above in connecting the ordinary electrical phenomena in these elements with the effects of heat, it seems almost certain that a further close connexion must exist between the electric actions and the specific heats of these elements.

I have to thank Dr. Thornton, Mr. R. Appleyard, Mr. E. E. Brooks and others for kind help and criticism in putting the above work into shape.

XCV. *A Simple Formal Solution of the General Equations of Elastic Stress.* By R. F. GWYTHER, M.A.*

THE solution given here is derived from those given in a previous paper on "An Analytical Discrimination of Elastic Stresses in an Isotropic Body" †.

1. The solutions indicated in that paper, in the case where no bodily forces are acting, may be briefly re-stated as follows:—

$$P = -\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\bar{\theta} - \frac{\partial^2\theta_3}{\partial y^2} - \frac{\partial^2\theta_2}{\partial z^2} \\ - \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\bar{\psi} + 2\frac{\partial^2\psi_1}{\partial y\partial z},$$

.... = ...

$$S = \frac{\partial^2\bar{\theta}}{\partial y\partial z} + \frac{\partial^2\theta_1}{\partial y\partial z} \\ + \frac{\partial^2\psi}{\partial y\partial z} + \frac{\partial^2\psi_1}{\partial z^2} - \frac{\partial^2\psi_2}{\partial x\partial y} - \frac{\partial^2\psi_3}{\partial x\partial z},$$

.... = ...

. (1)

* Communicated by the Author.

† Phil. Mag. July 1922, p. 274.

where

$$(m+n)\nabla^2\bar{\theta}=2m\left(\frac{\partial^2\theta_1}{\partial x^2}+\frac{\partial^2\theta_2}{\partial y^2}+\frac{\partial^2\theta_3}{\partial z^2}\right),$$

and

$$(m+n)\nabla^2\bar{\psi}=4m\left(\frac{\partial^2\psi_1}{\partial y\partial z}+\frac{\partial^2\psi_2}{\partial x\partial z}+\frac{\partial^2\psi_3}{\partial x\partial y}\right), \quad (2)$$

and where $\theta_1, \theta_2, \theta_3, \psi_1, \psi_2, \psi_3$ are Spherical Harmonic Functions.

The terms in the upper lines throughout, and in the lower lines throughout, form independent and general values of the elements of elastic stress.

If we write the components of bodily force per unit of mass in the form

$$\begin{aligned} -\frac{\partial V}{\partial x}-\frac{\partial W_3}{\partial y}-\frac{\partial W_2}{\partial z}, & \quad -\frac{\partial V}{\partial y}-\frac{\partial W_1}{\partial z}-\frac{\partial W_3}{\partial x}, \\ & \quad -\frac{\partial V}{\partial z}-\frac{\partial W_2}{\partial x}-\frac{\partial W_1}{\partial y}, \end{aligned}$$

we must then add ρV to the value of each P, Q, and R, and $\rho W_1, \rho W_2, \rho W_3$ to the values of S, T, U respectively given in (1) in order to satisfy the stress equations.

Since the equations are linear, we may consider each case separately, and collect the results.

Taking the terms in V, we may employ the solutions in the upper lines or in the lower lines of (1) indiscriminately, and write

$$\begin{aligned} P &= \rho V - \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \phi, \\ Q &= \rho V - \left(\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial x^2} \right) \phi, \\ R &= \rho V - \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \phi, \\ S &= \frac{\partial^2 \phi}{\partial y \partial z}, \quad T = \frac{\partial^2 \phi}{\partial x \partial z}, \quad U = \frac{\partial^2 \phi}{\partial x \partial y}, \quad \dots \quad (3) \end{aligned}$$

where the components of the displacement are given by

$$2nu = \frac{\partial \phi}{\partial x}, \quad 2nv = \frac{\partial \phi}{\partial y}, \quad 2nw = \frac{\partial \phi}{\partial z}, \quad \dots \quad (4)$$

and the only condition requisite that the stress may be elastic is that

$$(m+n)\nabla^2\phi=2n\rho V. \quad \dots \quad (5)$$

If, for example,

$$V = \int \frac{dM_1}{r_1},$$

then

$$\phi = \frac{n\rho}{m+n} \int r_1 dM_1.$$

The terms arising from V are now considered as completed.

Turning then to the terms in W , we shall find the solutions given in the lower lines the more convenient, and will write :

$$P = - \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \bar{\psi} + 2 \frac{\partial^2 \psi_1}{\partial y \partial z},$$

$$\dots = \dots$$

$$S = W_1 + \frac{\partial^2 \bar{\psi}}{\partial y \partial z} + \frac{\partial^2 \psi_1}{\partial x^2} - \frac{\partial^2 \psi_2}{\partial x \partial y} - \frac{\partial^2 \psi_3}{\partial x \partial z},$$

$$\dots = \dots,$$

$$\dots \dots \dots (6)$$

where

$$2nu = \frac{\partial \bar{\psi}}{\partial x} - 2 \frac{\partial \psi_3}{\partial y} - 2 \frac{\partial \psi_2}{\partial z}, \text{ etc. } \dots \dots (7)$$

The conditions requisite for elastic stresses are

$$(1) \text{ that } S = n \left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \text{ etc.,}$$

from which we find in turn

$$W_1 + \nabla^2 \psi_1 = 0, \quad W_2 + \nabla^2 \psi_2 = 0, \quad W_3 + \nabla^2 \psi_3 = 0; \quad (8)$$

$$(2) \text{ that } P - Q = 2n \left(\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} \right), \text{ etc.,}$$

which are satisfied identically,

$$\text{and } (3) \text{ that } P + Q + R = (3m - n) \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right),$$

whence

$$(m + n) \nabla^2 \bar{\psi} = 4m \left(\frac{\partial^2 \psi_1}{\partial y \partial z} + \frac{\partial^2 \psi_2}{\partial x \partial z} + \frac{\partial^2 \psi_3}{\partial x \partial y} \right). \dots (9)$$

2. The simplification which I am about to introduce arises from the substitution of a single term to stand for each of the expressions

$$\frac{\partial \psi_3}{\partial y} + \frac{\partial \psi_2}{\partial z}, \quad \frac{\partial \psi_1}{\partial z} + \frac{\partial \psi_3}{\partial x}, \quad \frac{\partial \psi_2}{\partial x} + \frac{\partial \psi_1}{\partial y}$$

in the values of $2nu$, etc., given in (7). However, guided

by experience gained in obtaining the foregoing results, I shall also alter the method of investigation by reversing the order of the steps, and shall secure that the elements of stress satisfy the conditions for being elements of elastic stress first, and that the stress equations are satisfied as the final step.

Accordingly I shall write

$$2nu = \frac{\partial \bar{\phi}}{\partial x} - 2\phi_1, \quad 2nv = \frac{\partial \bar{\phi}}{\partial y} - 2\phi_2, \quad 2nw = \frac{\partial \bar{\phi}}{\partial z} - 2\phi_3, \quad (10)$$

and

$$\begin{aligned} P &= -\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\bar{\phi} - \frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial y} + \frac{\partial \phi_3}{\partial z}, \\ Q &= -\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2}\right)\bar{\phi} + \frac{\partial \phi_1}{\partial x} - \frac{\partial \phi_2}{\partial y} + \frac{\partial \phi_3}{\partial z}, \\ R &= -\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\bar{\phi} + \frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial y} - \frac{\partial \phi_3}{\partial z}, \\ S &= \frac{\partial^2 \bar{\phi}}{\partial y \partial z} - \frac{\partial \phi_3}{\partial y} - \frac{\partial \phi_2}{\partial z}, \\ T &= \frac{\partial^2 \bar{\phi}}{\partial x \partial z} - \frac{\partial \phi_1}{\partial z} - \frac{\partial \phi_3}{\partial x}, \\ U &= \frac{\partial^2 \bar{\phi}}{\partial x \partial y} - \frac{\partial \phi_2}{\partial x} - \frac{\partial \phi_1}{\partial y} \dots \dots \dots (11) \end{aligned}$$

In this case the conditions that

$$\begin{aligned} S &= n\left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}\right), \quad T = n\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right), \quad S = n\left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\right), \\ P - Q &= 2n\left(\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y}\right), \quad P - R = 2n\left(\frac{\partial u}{\partial x} - \frac{\partial w}{\partial z}\right), \end{aligned}$$

are all satisfied identically, and the condition that

$$P + Q + R = (3m - n)\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right)$$

requires that

$$(m + n)\nabla^2 \bar{\phi} = 2m\left(\frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial y} + \frac{\partial \phi_3}{\partial z}\right) \dots \dots (12)$$

Substituting in the stress equation, we shall find, if X, Y, Z are the components of bodily force per unit of mass in excess of the terms already considered, viz.

$$\begin{aligned} &-\frac{\partial V}{\partial x}, \quad -\frac{\partial V}{\partial y}, \quad -\frac{\partial V}{\partial z}, \\ \nabla^2 \phi_1 &= \rho X, \quad \nabla^2 \phi_2 = \rho Y, \quad \nabla^2 \phi_3 = \rho Z. \dots (13) \end{aligned}$$

The equations (11) with the conditions (12) and (13) give the simple solution I have to offer, and the components of the displacement are given by (10). The basis of the simplification consists in the reduction of the degree of many of the differential coefficients as compared with the solutions as given by (1). Since the terms thus simplified do not enter the solutions embodied in (3) and (5), there is no simplification in that case.

In the case of a whirling body considered on page 283 of the paper previously referred to, the reversed effective forces have components, beyond those which may be included in

$$-\rho \frac{\partial V}{\partial x}, \quad -\rho \frac{\partial V}{\partial y}, \quad -\rho \frac{\partial V}{\partial z},$$

dealing with angular velocities, viz.

$$\rho(y\dot{\omega}_z - z\dot{\omega}_y), \quad \rho(z\dot{\omega}_x - x\dot{\omega}_z), \quad \rho(x\dot{\omega}_y - y\dot{\omega}_x),$$

dealing with the rates of change of the angular velocities. These will replace ρX , ρY , ρZ in (13), so that

$$\nabla^2 \phi_1 = \rho(y\dot{\omega}_z - z\dot{\omega}_y), \text{ etc.}$$

Since the solutions arising from bodily forces are Particular solutions, we may write

$$\phi_1 = \frac{1}{2} \rho x^2 (y\dot{\omega}_z - z\dot{\omega}_y), \text{ etc.,}$$

and so find

$$\frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial y} + \frac{\partial \phi_3}{\partial z} = 0,$$

and we may treat ϕ as null for the reason given above.

Hence from (11), in this case*,

$$P = -2\rho x(y\dot{\omega}_z - z\dot{\omega}_y), \text{ etc.,}$$

$$S = -\frac{1}{2} \rho \dot{\omega}_x (y^2 - z^2), \text{ etc.,}$$

$$\text{with } 2nu = -\rho x^2 (y\dot{\omega}_z - z\dot{\omega}_y), \text{ etc.,}$$

and the results are independent of the ratio m/n , while they satisfy the analytical conditions for elastic stresses.

When in (13) X , Y , Z are made null, we have the conditions that ϕ_1 , ϕ_2 , ϕ_3 shall be Spherical Harmonic Functions, and, with these additional conditions, equations (11) and (12) give the elastic stresses which are Complementary solutions when bodily forces are acting, and are the complete solutions when the body is subject to tractions only.

* This replaces an erroneous paragraph (the fourth) on page 283.

The full form of solution under general bodily forces will be collected from (3) and (11) with their respective conditions and with the Complementary solutions consequent on treating the bodily forces as null.

3. As an illustration of these Complementary solutions we may write

$$\phi_1 = \int \frac{dM_1}{r_1}, \text{ etc.,}$$

where $r_1^2 = (x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2$,

and $dM_1 = \rho_1 dx_1 dy_1 dz_1$

with the condition that r_1 shall never be zero, with corresponding expressions for ϕ_2 and ϕ_3 .

Then

$$\bar{\phi} = \frac{m}{m+n} \left\{ \int \frac{x-x_1}{r_1} dM_1 + \int \frac{y-y_2}{r_2} dM_2 + \int \frac{z-z_3}{r_3} dM_3 \right\}.$$

Retaining only the terms with subscript 1, we find a system of elastic stresses

$$\begin{aligned} P &= \frac{3m}{m+n} \int \frac{(x-x_1)^3}{r_1^5} dM_1 + \frac{n}{m+n} \int \frac{x-x_1}{r_1^3} dM_1, \\ Q &= \frac{3m}{m+n} \int \frac{(x-x_1)(y-y_1)^2}{r_1^5} dM_1 - \frac{n}{m+n} \int \frac{x-x_1}{r_1^3} dM_1, \\ R &= \frac{3m}{m+n} \int \frac{(x-x_1)(z-z_1)^2}{r_1^5} dM_1 - \frac{n}{m+n} \int \frac{x-x_1}{r_1^3} dM_1, \\ S &= \frac{3m}{m+n} \int \frac{(x-x_1)(y-y_1)(z-z_1)}{r_1^5} dM_1, \\ T &= \frac{3m}{m+n} \int \frac{(x-x_1)^2(z-z_1)}{r_1^5} dM_1 + \frac{n}{m+n} \int \frac{z-z_1}{r_1^3} dM_1, \\ U &= \frac{3m}{m+n} \int \frac{(x-x_1)^2(y-y_1)}{r_1^5} dM_1 + \frac{n}{m+n} \int \frac{y-y_1}{r_1^3} dM_1. \quad (14) \end{aligned}$$

4. Extension to general orthogonal coordinate systems.

It is clear that in these systems we may form expressions for the elements of stress and coordinates of displacement cognate to those for the cartesian system which are contained in equations (11), (12), and (13) and that a measure of simplification will result of the same general character as in the cartesian system though naturally less in degree.

Thus we should write

$$\begin{aligned}
 P &= -h_2^2 \frac{\partial^2 \phi}{\partial \eta^2} - h_3^2 \frac{\partial^2 \phi}{\partial \zeta^2} + h_1^2 \left(\frac{1}{h_2} \frac{\partial h_2}{\partial \xi} + \frac{1}{h_3} \frac{\partial h_3}{\partial \xi} \right) \frac{\partial \phi}{\partial \xi} \\
 &\quad - h_2 \left(\frac{\partial h_2}{\partial \eta} - \frac{h_2}{h_3} \frac{\partial h_3}{\partial \eta} \right) \frac{\partial \phi}{\partial \eta} - h_3 \left(\frac{\partial h_3}{\partial \zeta} - \frac{h_3}{h_2} \frac{\partial h_2}{\partial \zeta} \right) \frac{\partial \phi}{\partial \zeta} - e' + f' + g', \\
 &\dots = \dots\dots\dots \\
 S &= h_2 h_3 \frac{\partial^2 \phi}{\partial \eta \partial \zeta} + h_3 \frac{\partial h_2}{\partial \zeta} \frac{\partial \phi}{\partial \eta} + h_2 \frac{\partial h_3}{\partial \eta} \frac{\partial \phi}{\partial \zeta} - a', \quad \dots\dots\dots (15) \\
 &\dots = \dots\dots\dots
 \end{aligned}$$

and

$$2nu = h_1 \frac{\partial \phi}{\partial \xi} - 2\phi_1, \quad 2nv = h_2 \frac{\partial \phi}{\partial \eta} - 2\phi_2, \quad 2nw = h_3 \frac{\partial \phi}{\partial \zeta} - 2\phi_3, \quad (16)$$

where $\{e', f', g', a', b', c'\}$ are related to ϕ_1, ϕ_2, ϕ_3 as, in the usual notation of the subject, $\{e, f, g, a, b, c\}$ are related to u, v, w . The terms in ϕ in the expressions for the elements of stress are derived from the solutions of the Stress Equations as given by me *, when $\theta_1, \theta_2, \theta_3$ are each replaced by ϕ .

By making use of the expressions for the elements of strain, we may verify that

$$S = na, \quad T = nb, \quad U = nc,$$

$$P - Q = 2n(e - f), \quad P - R = 2n(e - g) \text{ are satisfied.}$$

The remaining condition to secure the elastic nature of the stress, namely

$$P + Q + R = (3m - n)(e + f + g),$$

becomes on substitution

$$\begin{aligned}
 (m + n) \nabla^2 \phi &= 2m(e' + f' + g') \\
 &= 2mh_1 h_2 h_3 \left\{ \frac{\partial}{\partial \xi} \left(\frac{\phi_1}{h_2 h_3} \right) + \frac{\partial}{\partial \eta} \left(\frac{\phi_2}{h_3 h_1} \right) + \frac{\partial}{\partial \zeta} \left(\frac{\phi_3}{h_1 h_2} \right) \right\}. \quad (17)
 \end{aligned}$$

If we now substitute for the elements of stress in the Stress Equations, the terms in ϕ will disappear, since they are known to satisfy identically the equations under tractions only, and the remaining terms contain ϕ_1, ϕ_2, ϕ_3 only.

The final quantities which are to be equated to $\rho X, \rho Y, \rho Z$,

* Phil. Mag. Sept. 1923, p. 482.

or to zero, as the case may be, become

$$\begin{aligned} \nabla^2 \phi_1 - \left\{ \frac{h_1^2}{h_2^2} \left(\frac{\partial h_2}{\partial \xi} \right)^2 + \frac{h_2^2}{h_1^2} \left(\frac{\partial h_1}{\partial \eta} \right)^2 + \frac{h_1^2}{h_3^2} \left(\frac{\partial h_3}{\partial \xi} \right)^2 + \frac{h_3^2}{h_1^2} \left(\frac{\partial h_1}{\partial \zeta} \right)^2 \right\} \phi_1 \\ - 2h_2 \frac{\partial h_1}{\partial \eta} \frac{\partial \phi_2}{\partial \xi} + 2h_1 \frac{\partial h_2}{\partial \xi} \frac{\partial \phi_2}{\partial \eta} - 2h_3 \frac{\partial h_1}{\partial \zeta} \frac{\partial \phi_3}{\partial \xi} + 2h_1 \frac{\partial h_3}{\partial \xi} \frac{\partial \phi_3}{\partial \zeta} \\ + \left\{ h_1 \frac{\partial^2 h_2}{\partial \xi \partial \eta} - h_2 \frac{\partial^2 h_1}{\partial \xi \partial \eta} + \frac{h_2}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_1}{\partial \eta} - \frac{h_1}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_2}{\partial \eta} \right. \\ \left. - \frac{h_1 h_2}{h_3^2} \frac{\partial h_3}{\partial \xi} \frac{\partial h_3}{\partial \eta} + \frac{h_2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial h_1}{\partial \eta} - \frac{h_1}{h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \eta} \right\} \phi_2, \\ + \left\{ h_1 \frac{\partial^2 h_3}{\partial \xi \partial \zeta} - h_3 \frac{\partial^2 h_1}{\partial \xi \partial \zeta} + \frac{h_3}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_1}{\partial \zeta} - \frac{h_1 h_3}{h_2^2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_2}{\partial \zeta} \right. \\ \left. - \frac{h_1}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial h_3}{\partial \zeta} + \frac{h_3}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_1}{\partial \zeta} - \frac{h_1}{h_2} \frac{\partial h_3}{\partial \xi} \frac{\partial h_2}{\partial \zeta} \right\} \phi_3, \quad (18) \end{aligned}$$

with two homologous expressions.

In spite of their length, these expressions constitute a very real simplification.

XCVI. *Convective Cooling in Liquids—Some Thermal Conductivity Data.* By A. H. DAVIS, M.Sc. (From the National Physical Laboratory*.)

THE author has recently given data † for the cooling of horizontal wires immersed in various liquids, and has correlated them, on the basis of hydrodynamical considerations, with the physical properties of the liquids concerned. In the work it was taken for granted that the thermal conductivities of the liquids were not markedly dependent upon temperature. However, C. W. Rice ‡, apparently by analysing results for these liquids on the basis of a modification of Langmuir's film theory of convection, has deduced § positive temperature coefficients equivalent to about 1 per cent. increase in conductivity per degree temperature rise.

* Communicated by the Director.

† Phil. Mag. xlv. p. 920 (1922).

‡ Phys. Rev. xxi. p. 474, 1923 (Abstract).

§ With regard to the basis of Rice's calculations, it is difficult to see why his equation for film thickness contains the acceleration (g) due to gravity, while it omits the volume coefficient of expansion (α) of the fluid and the temperature excess of the body. For presumably it is through the vigour of the convection (gravity) currents set up that ' g ' affects the film thickness; and ' α ' is as important as ' g ' in determining these.

Such effects are rather large and are of opposite sign to those the present author had reason to expect. It was desirable, therefore, to carry out direct determinations of thermal conductivity at various temperatures, to supplement the information already given concerning the liquids in question.

Fortunately, apparatus which had been used in the convection experiments was readily adaptable to comparisons of thermal conductivity by the Goldschmidt * method, and a test was therefore carried out.

Apparatus.

The method consisted in stretching a fine platinum wire along the axis of a narrow horizontal silver tube full of the test liquid, and measuring the electric current necessary to maintain a measured temperature difference between the wire and the walls of the tube. A relative value of the thermal conductivity was thus obtained.

In the actual apparatus the silver tube, 2 mm. diameter and 12.7 cm. long, was fitted tightly into a massive copper cylinder of 5 cm. diameter, so that the temperature was uniform throughout its length. The axial wire was 1 mil (0.002 cm.) in diameter. A shorter length of the same wire, passing through another silver tube in the block, was used for the automatic compensation of any end-effects. The whole apparatus was completely immersed in a vessel full of the liquid to be examined, which thus filled the capillary tube. The vessel itself was immersed in a carefully designed water-bath kept well-stirred at constant temperature.

Using a Wheatstone Bridge arrangement for the necessary resistance measurements, determinations were made of the heat dissipation associated with various small temperature excesses of the wire, ranging from 1° or 2° C. to 10° or 20° C. For moderate heating the results were almost completely independent of the temperature excess, whence it may be inferred that convection currents were inappreciable. The conductivity given later is the value to which results tended as the temperature excess was reduced.

Results.

For each liquid, experiments were carried out at two or three temperatures in the range 15° to 80° C. Provided the apparatus was not interfered with mechanically, values for the various temperatures were found to repeat accurately,

* *Phys. Zeits.* xii. p. 417 (1911).

deviations from the mean curve being generally less than 1 per cent. The relative values of the thermal conductivities of different liquids, however, were not reliable to better than ± 5 per cent., since the constant of the instrument changed within these limits when the apparatus was emptied, cleaned, and refilled.

Taking as standard the value given by Goldschmidt for toluol at air temperatures ($10^4 k = 3.42$) the mean results obtained have been summarized in Table I.

It appears that the thermal conductivity does not depend markedly upon the temperature of the liquid, and contrary to the calculations already referred to, the effect is generally a slight decrease as the temperature is raised.

I desire to thank Dr. G. W. C. Kaye for continuing the facilities afforded for the convection work. Mr. R. R. Strand assisted with the experimental arrangements and observations.

TABLE I.

Liquid.	Temperature (t).	Thermal Conductivity (cals. per cm. per $^{\circ}\text{C}$.) (k).	Temperature coefficient $\dagger$. (α).
Toluol	19 $^{\circ}$ C.	3.4×10^{-4}	} -0.002
	69	3.1	
Carbon tetra- chloride ...	23	2.8	} -0.003
	68	2.4	
Olive oil* ...	19	4.0	} -0.000 ₉
	71	3.85	
Aniline	15	4.4	} -0.000 ₃
	73	4.35	

* With olive oil progressive discoloration was noticed as time went on, and the measured values of the thermal conductivity increased from day to day, presumably owing to contamination with copper.

$\dagger k_t = k_0 (1 + \alpha t)$.

Note added February 1924.

Since this paper was written a more recent contribution by Rice (Am. I.E.E., J. xlii. p. 1288, Dec. 1923) has been published. His equations have now been modified to include the additional variables referred to above, and in consequence negative temperature coefficients of thermal conductivity have been calculated. These are in better agreement with the experimental values of the present paper.

The new equations, representing the latest development of the film hypothesis, contain all the variables required in a general hydrodynamical theory of convection. Even in a film theory hydrodynamical considerations seem unavoidable, since the size and characteristics of the film need to be explained.

XCVII. *Photoelectric and Photochemical Activity.* By O. W. RICHARDSON, F.R.S., *Wheatstone Professor of Physics, King's College, London*.*

THE formulæ developed by Kramers† and Milne‡ for the photoelectric activity of radiation in recent important papers have a very close connexion with formulæ which I obtained in 1911-13§ based, broadly speaking, on the same general type of ideas. The special features which link up the new formulæ with Bohr's theory are, of course, absent from mine, which originated independently of that theory and for the most part prior to the publication of it. The important formula is that expressed in equation (20), p. 224, of Milne's paper, which is the same as equation (17), p. 843, of Kramers. This is

$$\psi^{(r)}(\nu) = \frac{4\pi^2 m^2 \sigma \nu^2 F^{(r)}(\nu)}{q_r c} \left(\frac{c}{h\nu} \right)^3 = \frac{8\pi^2 \sigma m c^2 F^{(r)}(\nu)}{q_r} \frac{h\nu - \chi^{(r)}}{h^3 \nu^3}, \quad (1)$$

where $\psi^{(r)}(\nu)$ denotes the probability that an electron in the r th stationary state will be ejected from an atom in unit time by unit intensity of temperature radiation in the stretch ν to $\nu + d\nu$; q_r is the weight and σ the symmetry number of an electron in the r th state; $\chi^{(r)}$ is the corresponding ionization potential; and m , c , and h have their usual significance. $F^{(r)}(\nu)$ is the effective area of the appropriately ionized atom for capturing electrons moving with initial velocity v .

Let us compare this with the equation (5a) on p. 571 of *Phil. Mag.* Oct. 1912, which I give for a closely-related quantity, viz:—

$$\epsilon F(\nu) = \frac{A_1 h}{R^2 \nu^2} \left(1 - \frac{w_0}{h\nu} \right) = \text{const.} \times \frac{h\nu - \chi}{h^3 \nu^3} \dots \dots (2)$$

Here $\epsilon F(\nu)$ is the number of electrons emitted from unit area of a body having a single threshold given by $\chi = h\nu_0$

* Communicated by the Author.

† *Phil. Mag.* xvi. p. 836 (1923).

‡ *Phil. Mag.* xlvii. p. 209 (1924).

§ *Phil. Mag.* xxiii. p. 594 (1912), xxiv. p. 570 (1912), xxvii. p. 476 (1914).

per unit time per unit intensity of temperature radiation in the stretch ν to $\nu + d\nu$. The constant is independent of ν , v , T , and χ .

Equation (1) merges into (2), provided $F^{(v)}(v)$ is independent of v , or ν , of which it is in general a function through v . Now, the deduction of equation (2) involves the explicit assumption either that the proportion of the returning electrons which is reflected may be treated as negligible, or, if not negligible, at any rate independent of the temperature. Now, the temperature is proportional to the average value of $\frac{1}{2}mv^2$; so that either of these assumptions is equivalent to making the effective areas of the atoms for capturing electrons independent of v . This result is a direct consequence of the index 2 of T in equation (5) of the above paper, viz :—

$$\int_0^{\infty} \epsilon F(\nu) h\nu^3 e^{-\frac{h\nu}{RT}} d\nu = A_1 T^2 e^{-\frac{\chi_0}{RT}} \dots \dots (3)$$

If, however, we do not assume that the proportion of electron reflexions is independent of the temperature, but make other assumptions about the behaviour of this phenomenon, we arrive at quite different results, as can be seen by the general method which is developed more fully in *Phil. Mag.* vol. xxvii. p. 476 (1914). We may, for example, assume that the probability of a capture is inversely proportional to the square of the velocity (or to the equivalent quantity $h\nu - \chi$.) This is the assumption which Milne requires to account for the finite absorption in the region of the continuous spectrum just beyond the limits of spectral series, and which Eddington has shown is consistent with the limiting value for small velocities under the inverse square law of attractions. The equivalent assumption in the notation in which I was operating is that the quantity α in equation (2) of *Phil. Mag.* p. 570, vol. xxiv. (1912), which is the proportion of the returning electrons which are absorbed (not reflected), should vary as T^{-1} . This has the effect of altering the index 2 of T in equation (3) above to 1, with the result that, instead of (3), we have

$$\int_0^{\infty} \epsilon F(\nu) h\nu^3 e^{-\frac{h\nu}{RT}} d\nu = \text{const.} \times T e^{-\frac{\chi_0}{RT}} \dots \dots (4)$$

The solution of this by the same method is

$$\epsilon F(\nu) = 0, \quad 0 < h\nu < w_0, \quad \dots \dots (5)$$

$$\epsilon F(\nu) = \text{const.}/\nu^3, \quad w_0 < h\nu < \infty, \quad \dots \dots (6)$$

in agreement with Milne and Eddington for this case.

XCVIII. *Some Remarks on the Theory of Solutions.* By ANGUS F. CORE, *Chemical Department, The University, Manchester* *.

THE complete behaviour of a solution can only be deduced by a thorough application of statistical mechanical principles. Such a calculation would involve an exact knowledge of the interaction of the various species of molecule, and would in general be exceedingly complex. In default of such complete knowledge and analytical skill, progress has sometimes been attempted in the following way. The solute molecules have been considered as a gas, the complex interaction between the solute and solute, solute and solvent, and solvent and solvent molecules being for this purpose allowed for, necessarily somewhat roughly, by ascribing to the solute molecules alone an appropriate interaction, while the solvent is treated as a vacuum. The osmotic pressure of the solute is then deduced by calculating the external pressure of such a gas. The validity of this method was attacked by Mr. Cavanagh in the first of three articles on "Molecular Thermodynamics" (*Phil. Mag.* March 1922, p. 606). In the present paper it is sought to justify the "gas method" under certain conditions.

In the set of papers referred to, Mr. Cavanagh has elaborated an extension of Planck's thermodynamic method in his treatment of solutions. In this the thermodynamic potential of the solution is calculated in terms of the total energy and volume expressed as functions of the temperature, pressure, and composition. Mr. Cavanagh uses as components the various actual molecular species. If a knowledge of the properties of these molecules is presupposed, it might be possible to calculate the total energy and volume, and then, applying the thermodynamical relations, deduce the actual behaviour of the solution. Thus theory and experiment are brought into contact. The suggestion is made that, by measuring the colligative properties of the solutions of certain solutes in associating solvents, the degree of association of the solvent may be determined. An attempt is made in the present paper to show that this is not possible. The general question is raised as to the suitability of making the total energy and volume the connecting link between theory and experiment, and it is suggested that the use

* Communicated by Prof. S. Chapman.

of the activities or "fugacities" * of the components is preferable.

1. Consider a solution contained in a vessel. At any instant the solute molecules are in a definite statistical arrangement with respect to each other. We may now imagine a gas occupying an equal volume and containing the same number of molecules as solute molecules in the solution and at the same temperature. If the intermolecular actions of the gas molecules are such that at any instant their statistical arrangement is the same as that of the solute molecules, then we may define the gas as equivalent to the solute for the particular concentration, the solution being at a given temperature and under a given hydrostatic pressure. The actual forces experienced by a single solute molecule at any instant when the other solute molecules are in given positions will be quite different from the forces experienced by an equivalent gas molecule similarly situated with respect to the other gas molecules. These forces are equivalent to the statistical average effect on the solute molecule so situated for all the possible positions of the solvent molecules, the other solute molecules remaining in the given positions.

Now suppose that we increase the concentration and adjust the hydrostatic pressure on the solution so that it remains in osmotic equilibrium with pure solvent at constant pressure. If under these conditions the same gas molecules remain equivalent to the solute, it will be shown that the osmotic pressure of the solute must equal the pressure exerted by the equivalent gas for all concentrations at the given temperature.

Consider a gas contained in a large vessel to which is attached a second vessel separated from the first by a partition of such a nature that when a gas molecule crosses the partition into the second vessel an amount of work χ is expended. Then χ is the mechanical potential of the region

* If " f " is the fugacity of a component in a given molecular state in one system and " f' " its fugacity in another system at the same temperature, then the work required to transfer some of the component from the first system to the second isothermally and under conditions of constant pressure is equal to $RT \log f'/f$ per gram molecule. This, together with the statement that the fugacity of the isolated component in the given molecular condition and in the state of a gas is equal to the gas-pressure, completes the definition of fugacity. It is evident that the fugacity of a molecular species in a liquid mixture is equal to the vapour-pressure of the corresponding molecules if the vapour behaves as a perfect gas.

in the second vessel. We shall suppose that χ is so great that at the temperature of the gas the concentration of molecules, ν_1 , across the partition is sufficiently small for the gas to behave perfectly. Now let there be a similar arrangement containing the gas at a slightly different concentration, and let ν_2 be the concentration in the high-potential region. Then the work required to transfer the

gas from the one system to the other is $RT \log \frac{\nu_2}{\nu_1}$ per gram molecule. If C and $C+dC$, p and $p+dp$ are the concentrations and pressures in the two large vessels, then the work is also equal to dp/C per gram molecule. Therefore

$$\frac{\partial p}{\partial C} = RT \frac{\partial \log \nu}{\partial \log C}.$$

Now consider two exactly similar arrangements containing solutions of concentrations C and $C+dC$ and osmotic pressures π and $\pi+d\pi$, both in osmotic equilibrium with pure solvent at the same pressure. In this case, suppose that the partitions allow solvent to pass through perfectly freely, but that a solute molecule requires the work χ to pass through them. Let ν_1' and ν_2' be the molecular concentrations in the high-potential vessels. These are so small that we may assume that the osmotic pressure of the solute obeys the perfect gas laws. Then the work required to transfer solute from the concentration C to the concentration $C+dC$ is equal to $RT \log \frac{\nu_2'}{\nu_1'}$ per gram molecule. This work also equals $d\pi/C$. Therefore

$$\frac{\partial \pi}{\partial C} = RT \frac{\partial \log \nu'}{\partial \log C}.$$

We may now show that $\nu' = \nu$. For suppose that there are n molecules in the gas system. Then at any instant $n-1$ of these molecules are in definite positions. Consider a small region, dv , outside the influence of any of these $n-1$ molecules at the instant. Then there is a certain chance that the remaining molecule lies in this small region. This may be written $P_0 dv$. dv is a region of zero potential and P_0 is the same in every such region. The chance that the molecule lies in a unit of volume of the region of very high potential, χ , is therefore $P_0 e^{-\chi/kT}$. The total molecular concentration in the high-potential vessel is therefore given by

$$\nu = n P_0 e^{-\chi/kT}.$$

If there are also n molecules of solute in the solution, and the concentration is the same as that of the equivalent gas, then, since the statistical distribution is identical, the chance of a given solute molecule being in a small volume dr , in free solvent, that is outside the influence of any of the other solute molecules, is also $P_0 dr$. Therefore the concentration in the high-potential region is given by

$$\nu' = n P_0 e^{-\chi kT}.$$

Thus $\nu' = \nu$. It follows therefore that

$$\frac{\partial \pi}{\partial C} = \frac{\partial p}{\partial C}.$$

When C is very small, $\pi = p$. Therefore for all concentrations $\pi = p$.

We may identify the quantity $n P_0$ with the activity of the solute or gas.

The activity in these cases is defined so as to be equal to the actual concentration for very dilute conditions, and so that the work of transferring a gram molecule from a region of activity a to a region of activity a' is equal to $RT \log a'/a$. It will be perceived that both these conditions are satisfied by the quantity $n P_0$. Thus the activity of the equivalent gas is equal to the activity of the solute at the same concentration.

The activity of the solute as measured above is not quite equivalent to what is usually recorded as the activity of a solute. The difference in the logarithms of the activities of two solutions is usually identified with the work required to transfer a gram molecule of solute from the one solution to the other when the hydrostatic pressure on the solutions is the same. The activities we have considered refer to solutions maintained in equilibrium with free solvent at constant hydrostatic pressure. It seems to the writer that, from the point of view of theory, this is a more fundamental and more useful quantity, since its changes are not complicated by simultaneous changes in the potential of the free solvent.

The equality of p and π may be proved, perhaps, more directly as follows. Imagine parallel columns of the equivalent gas and solution in a vertical field of force. We may postulate that the field acts directly on the solute molecules and not on the solvent molecules; and that it acts with the same force on each gas molecule as it does on a single solute molecule. Suppose that the solution is limited below by a semi-permeable partition, beneath which is pure

solvent at a uniform pressure P in osmotic equilibrium with the solution. The columns of solution and gas are indefinitely extended in the upward direction. Let n be the number of solute molecules per unit area in the column above the semi-permeable partition, and let f be the force on each solute molecule exerted by the external field. The total force exerted by the field on the solution is therefore nf . Now raise the partition through a small vertical distance δx . The change effected by this is equivalent to raising the whole solution by δx and simultaneously transferring a certain quantity of solvent from a great height to the region under the partition. The work done therefore by this change against the external field is $n\delta x$ per unit area of the column. If π is the osmotic pressure just above the partition, the work done by the displacement is $\pi\delta x$ per unit area. Equating these two quantities, we obtain the relation $\pi = nf$. Similarly, if n' is the number of gas molecules per unit area above a level where the gas-pressure is p , then $p = n'f$. Now suppose that the gas is equivalent to the solute at all concentrations in solutions maintained in osmotic equilibrium with pure solvent at pressure P . Then, since the vertical column of solution is everywhere in equilibrium with pure solvent under a pressure P , it follows that the gas molecules will distribute themselves in exactly the same way as the solute molecules in the vertical field of force. Consequently $n' = n$. Therefore $\pi = p$.

The necessary and sufficient condition that this equality should hold is, then, that the same gas molecules should remain equivalent to the solute molecules for all concentrations of the solution when the hydrostatic pressure on the solution is adjusted so as to maintain the solution always in equilibrium with pure solvent under constant pressure. It is evident that no restriction is placed on the variation of the equivalent gas molecules with temperature, or on the variation of the volume of the solvent with temperature or pressure. It should be pointed out that this argument has no bearing on the "bombardment" theory of osmotic pressure. Whether the actual force on the membrane is the result of collisions with the solute molecules or not is of secondary importance, and must depend on the nature of the particular membrane used.

2. It is only in one or two very special cases that it is possible to say directly what is the approximate nature of the gas molecules which are equivalent to the solute molecules and so reduce the deduction of the osmotic pressure to

a problem in the kinetic theory of gases. It is sometimes supposed that the ions of a strong electrolyte behave in solution as though they acted on each other with forces varying inversely as the square of the distance between them. Although this assumption cannot be correct since it neglects the finite size of the solute and solvent molecules, nevertheless it is probably justifiable in the case of very dilute solutions. For these effects give rise to terms in the colligative properties of the solution which are proportional to a higher power of the concentration of the solute than that in the terms due to the electrostatic forces. The equivalent gas, then, consists of positively and negatively charged point molecules. If ϵ is the magnitude of the charge on each particle, the repulsion between two particles separated by a distance r is $+$ or $-\epsilon^2/Kr^2$ according to whether the particles have the same or opposite charges. K corresponds to the dielectric constant, and may be a function of the temperature without invalidating the method, but it must remain constant when the concentration of the solution is altered so long as this is maintained in osmotic equilibrium with pure solvent under constant pressure. If this is the case, we shall obtain the osmotic pressure of the electrolyte by calculating the pressure exerted by this equivalent gas. This may be done by calculating the activity of the gas or its virial, or, less naturally, by calculating the energy and applying the thermodynamic relation

$$p = T \int \frac{1}{T} \frac{\partial^2 U}{\partial v \partial T} dT - \left(\frac{\partial U}{\partial v} \right)_T.$$

In the integration there will occur a constant which gives rise to a term proportional to the temperature and to some function of the concentration. This term is equal to RT/r in the case of point molecules. In the integration the dielectric constant must be treated as independent of the temperature, even if in the solution it changes with the temperature.

Milner has calculated the virial of a gas consisting of point charges, and then obtained the pressure from the relation

$$pv = RT + \frac{1}{3}W.$$

In this, W is the virial and $1/v$ equals C , the total concentration of molecules of both signs. When the concentration is small,

$$W = -BC^{\frac{1}{2}},$$

and therefore

$$\pi = p = RTC - \frac{1}{3}BC^{\frac{3}{2}}.$$

In these

$$B = a\epsilon^3/R^{\frac{1}{2}}K^{\frac{1}{2}}T^{\frac{1}{2}},$$

“ a ” being a numerical constant.

An interesting case may be imagined in which the solute molecules are very large in comparison with the solvent molecules. In the liquid state the interaction between the different molecules may be such that over a wide range of temperature one solute molecule does not influence another solute molecule unless the distance between them is small compared with their linear dimensions. If the solute molecules are spherical and hard the equivalent gas will consist of hard non-attracting spheres. Therefore the osmotic pressure of the solute is given by

$$\pi = RTC + RTbC^2,$$

omitting terms proportional to a higher power of the concentration than the second. In this, b is equal to four times the actual volume of the molecules in a gram molecule of the solute. In this case the heat of dilution and the change of volume on dilution may be very slight, and yet Raoult's law of vapour-pressure will not be followed*.

3. We now turn to the thermodynamical treatment of solutions based on Planck's method. Consider for simplicity a mixture consisting of two molecular species only. Suppose that there are n_1 gram molecules of the first component and n_2 of the second. Let U be the total energy and V the total volume of the mixture. Then for the pure component 1 we may write

$$U = n_1 u_1, \quad V = n_1 v_1,$$

in which u_1 and v_1 depend on the temperature and pressure only. Now if we add a very little of component 2 so that

* All that is required here is that such a state of affairs should be possible. Nevertheless, to prevent possible misunderstanding, it may be pointed out that it is not at all a probable condition. However large a molecule is, it is still only a single molecule, and therefore, in order that the influence of one solute molecule on another should be negligible, it is necessary that the potential of the effective forces between them should be small compared with kT , k being the gas constant for a single molecule. The changes of potential energy associated with the variation of the modification in the solvent as two large solute molecules approach each other will probably be very far from small compared with kT , even when they are separated by a distance which is not small compared with their linear dimensions.

n_2 is very small compared with n_1 , we may assume that the following linear relation holds :

$$U = n_1 u_1 + n_2 u_2 ; \quad V = n_1 v_1 + n_2 v_2.$$

In these u_2 and v_2 are independent of everything except the temperature and pressure. These linear relations will be followed in all states of the mixture, gaseous or liquid. When the concentration of 2 is not very small, it is necessary to add extra terms to these expressions. Assume that it is possible to write them in the very general form * :

$$U = n_1 u_1 + n_2 u_2 + n_1 \sum u'_x f_x(c),$$

$$V = n_1 v_1 + n_2 v_2 + n_1 \sum v'_x f_x(c).$$

In these expressions c is written for n_2/n_1 . u' and v' depend only on the temperature and pressure, and $f'_x(c)$ only on the composition. We may now calculate the Planck potential function

$$\psi = -(U + PV)/T + \int (dU + PdV)/T + \text{a constant.}$$

Suppose that the integration is carried out under conditions of constant composition. The constant is then independent of the temperature and pressure, and is some function of the composition. To evaluate this constant we may start with the mixture when very rarefied and at a high temperature, in which state it will approximate to a perfect gas mixture, and then, by changing the temperature and pressure, convert the gas continuously into the liquid condition at the required temperature and pressure. We may then write,

$$\psi = \psi_{\text{gas}} - \left[(U + PV)/T \right]_{\text{gas}}^{\text{liquid}} + \int_{\text{gas}}^{\text{liquid}} (dU + PdV)/T.$$

Now let

$$\phi_1 = -(u_1 + Pv_1)/T + \int (du_1 + Pdv_1)/T + l_1,$$

$$\phi_2 = -(u_2 + Pv_2)/T + \int (du_2 + Pdv_2)/T + l_2,$$

$$\phi'_x = -(u'_x + Pv'_x)/T + \int_{\text{gas}}^{\text{liquid}} (du'_x + Pdv'_x)/T.$$

* Cavanagh, "Molecular Thermodynamics," Phil. Mag. xliii. p. 606 (1922).

In these expressions l_1 and l_2 are independent of both temperature and pressure, and also of the composition of the mixture. For the gas state the value of ψ is given by

$$\psi_{\text{gas}} = n_1\phi_1 + n_2\phi_2 - Rn_1 \log \frac{n_1}{n_1 + n_2} - Rn_2 \log \frac{n_2}{n_1 + n_2}.$$

Therefore in the liquid state we may write

$$\psi = n_1\{\phi_1 + R \log(1+c)\} + n_2\left\{\phi_2 + R \log \frac{c}{1+c}\right\} + n_1 \Sigma \phi_x / f_x(c).$$

From this we may deduce the osmotic pressure. For moderately small values of c the osmotic pressure of component 2 is given by

$$\pi = \frac{T}{v_1} \left\{ R \log(1+c) + \Sigma \phi_x' \left(f_x(c) - c \frac{\partial f_x(c)}{\partial c} \right) \right\}.$$

Suppose now that the solute is a strong electrolyte. According to the theory of complete ionization, the electrostatic forces will give rise to a term in the osmotic pressure when the solution is very dilute proportional to the concentration to the power of $3/2$. For very dilute solutions we may therefore neglect terms involving higher powers of c . Only to this degree of approximation may we assume that the "extra" terms in the expression for the potential are fully represented by the electrostatic effect. To this degree of approximation Milner showed that the electrostatic energy of the ions is given by

$$E = -BC^{\frac{1}{2}},$$

in which, as before,

$$B = a\epsilon^3 / R^{\frac{1}{2}} K^{\frac{3}{2}} T^{\frac{1}{2}}.$$

In this particular case the electrostatic energy is equal to the virial. C is the ordinary volume concentration. In terms of the concentration c , that is n_2/n_1 , this becomes to the necessary degree of approximation

$$E = -Bv_1^{-\frac{1}{2}} c^{\frac{1}{2}}.$$

This is the electrostatic energy per gram molecule. We shall first assume that the dielectric constant, K , and the molecular volume v_1 , are independent of the temperature. If this is so, the total energy of the solution may be written

$$U = n_1 u_1 + n_2 u_2 - n_1 B v_1^{-\frac{1}{2}} c^{\frac{1}{2}}.$$

It is also assumed that for all conditions

$$V = n_1 v_1 + n_2 r_2.$$

If these values be substituted in the relation given above, we obtain for the osmotic pressure to the required degree of approximation

$$\pi = TF(c) - \frac{1}{3} B v_1^{-\frac{2}{3}} c^{\frac{2}{3}}.$$

When the charges on the ions are reduced to zero, then to the same approximation the osmotic pressure becomes RTc/v_1 . Therefore $F(c) = Rc/v_1$, and

$$\pi = RT v_1^{-1} c - \frac{1}{3} B r_1^{-\frac{2}{3}} c^{\frac{2}{3}}.$$

In terms of the volume concentration C , this becomes

$$\pi = RTC - \frac{1}{3} B C^{\frac{2}{3}}.$$

This necessarily agrees with the result obtained by calculating the pressure of the equivalent gas consisting of charged point molecules.

In the above deduction, K and v_1 were treated as independent of the temperature. If we had used the same value for the total energy and allowed for dK/dT and dv_1/dT , a different result would have been obtained for the osmotic pressure. But, as we have seen, it should be the same, for when calculated from the pressure of the equivalent gas, the result is independent of the variation of K and v_1 with the temperature. The explanation of this is that, when K and v_1 vary with the temperature, it is incorrect to suppose that the total energy of the solution is obtained by adding the electrostatic potential energy of the ions, calculated as if K and v_1 were constant, to the total energy which would exist apart from the charges on the ions.

Consider two small bodies, each carrying the charge e , at a distance r from each other in a medium of dielectric constant K . The potential energy is $-\epsilon^2/Kr$. If the bodies move so that the distance between them increases by δr , and if the volume of the medium is independent of r , then the "maximum work" of the change is given by

$$A = -\epsilon^2 \delta r / Kr^2.$$

If K is independent of the temperature, then $-A = \delta U$, the change in the total energy U . If K varies with the temperature, then heat will be evolved or absorbed during the displacement of the charges and A will not equal $-\delta U$.

The thermodynamic relation is

$$\delta U = T^2 \left(\frac{\partial A/T}{\partial T} \right)_{\delta r}.$$

Therefore in this case

$$U = B - \frac{\epsilon^2}{K r} \left(1 - \frac{\partial \log K}{\partial \log T} \right),$$

where B is some quantity independent of r . The change in the last term during an isothermal change represents the heat evolved or absorbed from the medium.

In order to calculate the total energy of the electrolytic solution, consider the maximum work of transferring δn_1 gram molecules of solvent from the solution of composition n_1, n_2 to the pure solvent under the same pressure. If the solution is incompressible, this is given by

$$A = -\pi v_1 \delta n_1.$$

Substituting this in the relation between A and δU , and using the value of the osmotic pressure equal to the pressure of the equivalent gas, we obtain

$$U = n_1 u_1 + n_2 u_2 - n_1 B r_1^{-1} c^{\frac{1}{2}} \left(1 - \frac{1}{3} \frac{\partial \log K^{\frac{3}{2}} r_1}{\partial \log T} \right).$$

Mr. Cavanagh seeks to disprove the validity of the "virial method" in his first paper. He considers an imaginary case in which the virial is proportional to $c^{\frac{1}{2}}$, and assumes that the extra energy of the solution due to the charges on the ions is then equal to the virial. Comparing the osmotic pressure obtained with this assumption with that obtained from the virial, certain impossible consequences follow. The virial of a gas is, however, equal to the potential energy only in the case when the forces between the molecules varies inversely as the square of the distance, and in that case when sufficiently rarefied it is proportional to $C^{\frac{1}{2}}$ and not to $C^{\frac{1}{3}}$. Moreover, as we have just seen, the extra energy of the solution which is to be used in the calculation of the thermodynamic potential equals the electrostatic potential energy of the ions only if the dielectric constant and the gram molecular volume of the solvent are independent of the temperature.

In the same paper Mr. Cavanagh proposes a method for estimating the degree of association of a solvent by measuring the colligative properties of a solution. Without affecting the argument, we shall assume that this is the

osmotic pressure of the solution. The measurement of the solubility of a gas is the experiment actually proposed. The use of a "perfect" solute is essential to the method.

In a very dilute solution for all conditions whether liquid or gaseous, we may assume that

$$U = n_1 u_1 + n_2 u_2,$$

$$V = n_1 v_1 + n_2 v_2.$$

All the quantities $f_x(c)$ are negligible. Planck's potential function is therefore given by

$$\psi = n_1 \phi_1 + n_2 \phi_2 - R n_1 \log \frac{n_1}{n_1 + n_2} - R n_2 \log \frac{n_2}{n_1 + n_2}.$$

From this we may deduce the colligative properties. In particular the osmotic pressure

$$\pi = \frac{RT}{v_1} \log \left(1 + \frac{n_2}{n_1} \right).$$

It is evident that we have no right to use any term involving a higher power of the composition than the first. The above expression is, therefore, equivalent to

$$\pi = \frac{RT}{v_1} \frac{n_2}{n_1}.$$

This is essentially Planck's treatment in his thermodynamics. Everything depends on the necessity for the linear relationship of U and V with the composition. Now suppose that even for more concentrated solutions this linear relation holds for all conditions of the mixture from that of a liquid. Then for incompressible solutions we should have accurately within the range of concentration for which the linear relation holds

$$\pi = \frac{RT}{v_1} \log \left(1 + \frac{n_2}{n_1} \right).$$

In this case the mixture is called a perfect one. As far as terms of the second order, this may be written

$$\pi = RTC + RT(v_2 - \frac{1}{2}v_1)c^2.$$

In this expression, C is the ordinary volume concentration. If the solvent consists of several molecular species, and if the energy and volume relations are linear in respect of the molecular concentration of the solute, then it is shown that for moderately small concentrations

$$\pi = RTC + RT(v_2 - \frac{1}{2}\bar{v}_1)c^2,$$

even if the equilibrium between the solvent species is

influenced by the presence of the solute. In this expression r_1 is equal to $\bar{m}_1/\rho$, m_1 being the average molecular weight of the solvent and ρ its density. It is therefore evident that if we were in possession of a guaranteed perfect solute, then by measuring π we could deduce the value of $\bar{m}$ and therefore the degree of association of the solvent. But a perfect solute can only occur when very special conditions are fulfilled. When the two components of a binary mixture are exactly alike, they must certainly form a perfect mixture; the expressions for U and V must be linear with respect to n_1 and n_2 under all conditions. A mixture of two isotopes practically fulfils this condition unless, perhaps, when the temperature is very low. When the components are like each other, as in the case of benzene and toluene, a close approximation to a perfect mixture results. For a nearly perfect mixture the heat of dilution and the change of volume on dilution with either component must be very small over a wide range of temperature. It is important to notice that the converse of this is not necessarily true. The linearity of U and V with respect to n_1 and n_2 may be nearly true in the liquid condition, but not throughout all the stages between the gas condition and the liquid condition. In that case the liquid will not behave as a perfect mixture. The value of the integral

$$\Sigma \int_{\text{gas}}^{\text{liquid}} (du_r' + Pdv_r')/T$$

is not zero, but an unknown constant. This will give rise to a term in the osmotic pressure which is proportional to the temperature and to some probably complex function of the concentration. An ideal example of this is that of the large spherical solute molecules considered previously. In a general way it may be said that such cases occur if, while a certain balance exists between the attractions of solute for solute, solute for solvent, and solvent for solvent, yet the volume occupied by a solute molecule is very different from that occupied by a solvent molecule.

Suppose it was found in the case of a certain binary liquid mixture that the osmotic pressure of one component for all compositions throughout the complete range could be expressed by the simple relation

$$\pi = \frac{RT}{c_1} \log \left(1 + k \frac{M_2}{M_1} \right),$$

in which M_1 and M_2 are the masses of the two components in

the mixture and k is a constant ; or that the other colligative properties of the solution followed the correspondingly simple laws. Then we could say with confidence that k is the ratio of the molecular weight of the two components as they occur in the mixture. Moreover, we should conclude that the degree of polymerization, if any existed, of either component remained constant throughout the complete range of composition. Suppose, however, that this simple behaviour is not observed throughout the whole range ; and such behaviour would seem to be impossible when one of the components is an associating substance such as water. Then when the solution is exceedingly dilute, the osmotic pressure is RTC . From this it is possible to deduce simply the association of the solute. As the concentration is increased, the osmotic pressure will diverge from this, but there is no reason whatsoever for supposing that the second-order correction term will approximate to that proper to the perfect mixture after allowing for solvation and association. For the perfect mixture it is $RT(v_2 - \frac{1}{2}v_1)C^2$; for the large spherical solute molecules considered before, it is $RTbC^2$. It is necessary to suppose that, unless the mixture behaves perfectly throughout, the term is a complex function of the parameters defining the two kinds of molecule concerned. Thus in cases where there is reason to suppose that there is no solvation of the solute molecules and also no direct action between these, as for example in the case of a gas like argon dissolved in water, it is not justifiable to assume that the second term is equal to $RT(v_2 - \frac{1}{2}v_1)C^2$, and then from this to deduce the degree of association of the solvent. These remarks apply even if the heat of dilution and volume change on dilution are small.

5. Planck's method of deducing the colligative properties of solutions has led sometimes to misunderstanding concerning the occurrence and nature of perfect mixtures and the factors which cause departure therefrom. It would appear to be preferable to start with the relation between the fugacity and the concentration. There is exactly the same necessity for asserting that the fugacity of a definite molecular species is proportional to the concentration for all states of the mixture in the limit as the dilution is indefinitely increased, as there is for asserting that the energy and volume expressions are linear with respect to the composition. The other properties can then be deduced very simply.

Attempts have been made to carry the calculation of the colligative properties of solutions of strong electrolytes to a

stage further than Milner carried it. Allowance has been made for the finite size of the ions in deducing the energy introduced by the electrostatic attractions between them. The potential function is then calculated from the expression

$$\psi = n_1 \{ \phi_1 + R \log(1+c) \} + n_2 \left\{ \phi_2 + R \log \frac{c}{1+c} \right\} + n_1 \Sigma \phi'_x f_x(c).$$

It is incorrect to assume that the last term is entirely accounted for by these electrostatic effects, so that if the charges were reduced to zero the solution would behave as a perfect one. For in taking account of the finite size of the ions, terms are introduced which involve the square of the concentration or higher powers. If the ions are as large as these theories demand, the departure from perfect behaviour may be appreciable even at moderate concentrations, quite apart from the electrostatic effects.

The foregoing points have been emphasized because they illustrate the disadvantages of using the relationship of the total energy and volume of a mixture with the composition as a starting-point for the thermodynamical treatment. The volume of a liquid solution is frequently very nearly linear with respect to the composition, and in certain cases the total energy is either linear or contains an extra term, which can be calculated approximately as in the case of a solution of a strong electrolyte. But, as we have seen, this is not sufficient whereby to calculate the properties of the solution. In the expression for the osmotic pressure a term nearly proportional to the temperature and to a possibly complex function of the concentration is not associated with any appreciable quantity in the energy expression of the solution, and cannot be calculated from an approximate value of the energy. The principal object of formulating a thermodynamical treatment of a mixture of molecular species is to enable us to join theory to experiment—to build a bridge between them, so that from the dynamical theory we can calculate the actual behaviour of the mixture. From the dynamical theory it would then appear proper to calculate the fugacities or activities directly rather than the total energy and volume. Moreover, the former can be readily deduced from experimental results, and in some cases measured directly.

Chemical Department,
The University, Manchester,
February 1924.

XCIX. *Calculations of the Potential Energy for some Atomic Models.* By IDA WOODWARD*.

THE atomic models which form the basis of the following calculations are chosen for their simplicity; they consist of a positive nucleus surrounded by layers of electrons at rest. These electrons are divided into groups, all members of a group being at equal, or nearly equal, distances from the nucleus, and the electrons of a group are said to form a layer. As the two electrons which lie nearest to the nucleus are more intimately connected with it than are the remaining electrons, they are considered with the nucleus; this combination, which is generally spoken of as the atom, is regarded as a positive point charge, the magnitude of which is equal to the sum of the charges on the remaining electrons. If the number of these electrons be n , the charge on the atom is ne , where e has its usual significance, and denotes the magnitude of the electronic charge. Such an atom has the atomic number $(n+2)$.

The electrons in each layer are supposed to be distributed with as much symmetry as is geometrically possible, and the work is much simplified by this consideration. All values between one and eight are given to n , and the values 12 and 22 are considered in addition. For $n=1, 2$, and 4 , all the electrons are supposed to lie in one layer. For $n=3$, the case in which the electrons lie on a straight line is considered as well as that in which they form one layer. For $n=5, 6, 7$, and 8 , two cases are considered—that in which the electrons form one layer, and that in which they form two. For $n=8$, alternative distributions in the layers are considered. For $n=12$, two cases are considered, in each of which the electrons lie in two layers: in one case each of these layers contains 6 electrons, in the other they contain 8 and 4 electrons respectively. For $n=22$, the electrons are supposed to lie in three layers, containing (i.) 8, 8, and 6 electrons, (ii.) 8, 12, and 2 electrons. The number of electrons in the innermost layer is given first.

On account of the complexity of the equations obtained, an approximate solution only was found in more complicated cases.

The law of force assumed was everywhere as follows:—

Between an atom and an electron, an attraction $Ee\left(\frac{1}{r^2} - \frac{c}{r^3}\right)$.

Between two electrons, a repulsion $\frac{e^2}{r^2}$,

* Communicated by Sir J. J. Thomson, O.M., F.R.S.

where r is the distance between the charges under consideration, E the charge on the atom, and c an unknown quantity, constant for any particular atom.

The results show the comparative stability of various atomic models.

V is used throughout to denote the potential energy of the atom with its associated electrons.

I. Atom with one electron.

$$n=1, E=e.$$

There is here only one possible model.

Let a be the distance between the atom and the electron.

$$\begin{aligned} V &= -Ee \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\} \\ &= -e^2 \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\}. \end{aligned}$$

The condition for equilibrium is $\frac{dV}{da} = 0$.

$$\text{Hence} \quad a = c,$$

$$\text{and} \quad V = -\frac{e^2}{c} \times \frac{1}{2}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

II. Atom with two electrons.

$$n=2, E=2e.$$

Electrons and atom on the same straight line, the electrons being equidistant from the atom.

Let a = distance of electrons from atom.

$$\begin{aligned} V &= -2Ee \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\} + \frac{e^2}{2a} \\ &= -\frac{3 \cdot 5e^2}{a} + \frac{2ce^2}{a^2}. \end{aligned}$$

The condition of equilibrium $\frac{dV}{da} = 0$ gives

$$3 \cdot 5 = 4c/a.$$

$$\therefore a = 4c/3 \cdot 5 = 1 \cdot 143,$$

$$\begin{aligned} \text{and} \quad V &= \left\{ -\frac{(3 \cdot 5)^2}{4c} + \frac{2(3 \cdot 5)^2}{16c} \right\} e^2 \\ &= -1 \cdot 53125 \cdot \frac{e^2}{c}. \quad . \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

III. *Atom with three electrons.*

$$n=3, E=3e.$$

(i.) *One layer.*—Electrons at corners of an equilateral triangle, atom at its centroid.

Distance of electron from atom = a .

$$V = -3e^2 \left\{ \frac{3}{a} - \frac{3c}{2a^2} \right\} + \frac{3}{2} \cdot \frac{2}{\sqrt{3}} \frac{e^2}{a}.$$

For equilibrium, $\frac{dV}{da} = 0$.

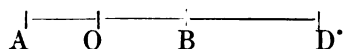
$$\therefore -\frac{7 \cdot 268}{a^2} + \frac{9c}{a^3} = 0,$$

$$\therefore \frac{c}{a} = .8076, \quad a = 1 \cdot 238c,$$

$$\text{and} \quad V = -\frac{e^2}{c} \times 2 \cdot 934. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(ii.) *Electrons and atom in one straight line.*

Atom at O, electrons at A, B, D.



Let $OA = a$, $OB = b$, $OD = d$.

$$V = -3e^2 \left\{ \frac{1}{a} + \frac{1}{b} + \frac{1}{d} - \frac{c}{2a^2} - \frac{c}{2b^2} - \frac{c}{2d^2} \right\} + e^2 \left\{ \frac{1}{b+a} + \frac{1}{a+d} + \frac{1}{d-b} \right\}. \quad . \quad . \quad (4)$$

The conditions of equilibrium, $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial c} = 0$, give the equations

$$\frac{3}{a^2} - \frac{3c}{a^3} - \frac{1}{(a+b)^2} - \frac{1}{(a+d)^2} = 0, \quad . \quad . \quad . \quad (5)$$

$$\frac{3}{b^2} - \frac{3c}{b^3} - \frac{1}{(a+b)^2} + \frac{1}{(d-b)^2} = 0, \quad . \quad . \quad . \quad (6)$$

$$\frac{3}{d^2} - \frac{3c}{d^3} - \frac{1}{(a+d)^2} - \frac{1}{(d-b)^2} = 0. \quad . \quad . \quad . \quad (7)$$

Neglecting a/d and b/d , equation (7) gives $d = 3c$.

If we try the solution

$$a = (1+x)c, \quad b = (1+y)c, \quad d = 3(1+z)c,$$

and neglect squares and higher powers of x , y , and z , we obtain the equations :

$$-10 + 105x + 8y + 3z = 0, \quad . \quad . \quad . \quad (8)$$

$$x + 14y - 3z = 0, \quad . \quad . \quad . \quad (9)$$

$$-26 + 9x - 72y + 147z = 0. \quad . \quad . \quad . \quad (10)$$

Hence $x = .087, \quad y = .035, \quad z = .192,$

$$\text{and } \left. \begin{aligned} a &= 1.087c, \\ b &= 1.035c, \\ c &= 3.577c. \end{aligned} \right\} . \quad . \quad . \quad . \quad (11)$$

Substituting in (4), it is found that

$$V = -\frac{e^2}{c} \times 2.7868. \quad . \quad . \quad . \quad (12)$$

IV. Atom with four electrons.

$$n=4, E=4e.$$

One layer.—Electrons at corners of a regular tetrahedron, atom at its centre of volume.

Distance of electrons from atom = a .

$$V = -4 \times 4e^2 \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\} + \frac{4}{2} \times \frac{3}{1.633a}. \quad . \quad (13)$$

The condition of equilibrium $\frac{dV}{da} = 0$ is

$$\frac{12.3256}{a^2} - \frac{16c}{a^3} = 0.$$

$$\therefore \frac{c}{a} = .7704, \quad a = 1.298c, \quad . \quad . \quad . \quad (14)$$

$$\text{and } V = -\frac{e^2}{c} \times 4.748. \quad . \quad . \quad . \quad (15)$$

V. Atom with five electrons.

$$n=5, E=5e.$$

(i.) *One layer.*—Three electrons at the corner of an equilateral triangle, the atom lying at its centroid ; two electrons at equal distances from the atom, on a line through it perpendicular to the plane of the triangle.

Distance of each of the three electrons from atom = a .Distance of each of the two electrons from atom = b .

$$V = -5 \left\{ \frac{3}{a} + \frac{2}{b} - \frac{3c}{2a^2} - \frac{2c}{2b^2} \right\} + \frac{2 \times 3}{\sqrt{a^2 + b^2}} + \frac{1}{2b} + \frac{3 \times 2}{2\sqrt{3}a} \quad \dots (16)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, give

$$\frac{13 \cdot 268}{a^2} - \frac{6a}{(a^2 + b^2)^{3/2}} - \frac{15c}{a^3} = 0, \quad \dots (17)$$

$$\frac{9 \cdot 5}{b^2} - \frac{6b}{(a^2 + b^2)^{3/2}} - \frac{10c}{b^3} = 0. \quad \dots (18)$$

Eliminating c , and putting $\frac{b}{a} = x$, we get

$$4 \cdot 423 - 4 \cdot 75x - \frac{(2 - 3x^4)}{(1 + x^2)^{3/2}} = 0. \quad \dots (19)$$

A graphical solution of (19) gives

$$x = 1 \cdot 026.$$

Hence we find $\frac{c}{b} = 7 \cdot 265$, $\frac{c}{a} = 7 \cdot 454$.Therefore $a = 1 \cdot 342c$, $b = 1 \cdot 376c$. $\dots (20)$

$$\text{and } V = -\frac{e^2}{c} \times 6 \cdot 806. \quad \dots (21)$$

(ii.) *Two layers*.—Atom at origin of Cartesian coordinates.
electrons at $(0, 0, a)$, $(0, 0, d)$, $(0, b, -f)$, $(\pm \frac{1}{2}\sqrt{3}b, -\frac{b}{2}, -f)$.
This corresponds to a system in which four electrons lie at the corners of a tetrahedron, and the fifth on a line drawn from the atom to one corner of the tetrahedron and produced.

$$V = -5 \left\{ \frac{3}{\sqrt{b^2 + f^2}} - \frac{3c}{2(b^2 + f^2)} + \frac{1}{a} + \frac{1}{d} - \frac{c}{2f} - \frac{c}{2f^2} \right\} \\ + \frac{3}{2} \times \frac{2}{\sqrt{3}} + \frac{3}{\sqrt{b^2 + (a+f)^2}} + \frac{3}{\sqrt{b^2 + (d+f)^2}} + \frac{1}{f}.$$

The conditions of equilibrium $\frac{\partial V}{\partial a}=0$, $\frac{\partial V}{\partial b}=0$, $\frac{\partial V}{\partial d}=0$, $\frac{\partial V}{\partial f}=0$, give

$$\frac{15b}{(b^2+f^2)^{3/2}} - \frac{1.732}{b^2} - \frac{3b}{(b^2+(a+f)^2)^{3/2}} - \frac{3b}{(b^2+(d+f)^2)^{3/2}} - \frac{15c \cdot b}{(b^2+f^2)^2} = 0, \quad (23)$$

$$\frac{15f}{(b^2+f^2)^{3/2}} - \frac{3(a+f)}{(b^2+(a+f)^2)^{3/2}} - \frac{3(d+f)}{(b^2+(d+f)^2)^{3/2}} - \frac{15f \cdot c}{(b^2+f^2)^2} = 0, \quad (24)$$

$$\frac{5}{a^2} - \frac{3(a+f)}{(b^2+(a+f)^2)^{3/2}} + \frac{1}{(d-a)^2} - \frac{5c}{a^3} = 0, \quad (25)$$

$$\frac{5}{d^2} - \frac{3(d+f)}{(b^2+(d+f)^2)^{3/2}} - \frac{1}{(d-a)^2} - \frac{5c}{d^3} = 0. \quad (26)$$

Neglecting powers of a/d , b/d , f/d and putting $a=b$, we obtain an approximate solution which suggests the trial solution :

$$a/c = 1.1(1+x),$$

$$b/c = 1.1(1+y),$$

$$f/c = .4(1+w),$$

$$d/c = 5(1+z),$$

where x , y , z , and w are supposed small and their squares and higher powers neglected.

Substituting in equations (23) to (26) and expanding, we get

$$-.1410 + .2222x + 1.4589y + .2371w + .01594z = 0,$$

$$-.0838 + .0624x + .7144y + .3072w + .0562z = 0,$$

$$-.2582 + 3.2284x + .7335y + .1772w - .1685z = 0,$$

$$+.00055 - .03709x + .01157y + .0135w - .0553z = 0.$$

Hence $x=.031$, $y=.120$, $w=-.192$, $z=.002$.

Therefore $a=1.134c$, $b=1.232c$, $f=.322c$, $d=5.105c$,

$$\text{and } V = -\frac{e^2}{d} \times 6.6672. \quad (27)$$

The distances of the electrons from the atom are readily found to be

$$\left. \begin{array}{l} 1.273c \text{ (three electrons),} \\ 1.134c \text{ (one electron),} \\ 5.105c \text{ (one electron).} \end{array} \right\} \quad \dots \quad (28)$$

a result which shows the amount of distortion produced by the atom lying outside on the inner layer.

VI. Atom with six electrons.

$$n=6, E=6e.$$

(i.) *One layer.*—Atom at $(0, 0, 0)$, electrons at $(\pm a, 0, 0)$, $(0, \pm a, 0)$, $(0, 0, \pm a)$. The atom is at the centre, and the electrons are at the centres of the faces, of a cube of edge $2a$.

$$V = -36e^2 \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\} + \frac{6}{2} \times \frac{3.328}{a} \cdot e^2 \quad \dots \quad (29)$$

The condition of equilibrium $\frac{dV}{da} = 0$ gives

$$\frac{c}{a} = \frac{13.008}{18}, \quad a = 1.385c. \quad \dots \quad (30)$$

$$\text{Hence} \quad V = -\frac{e^2}{c} \times 9.40. \quad \dots \quad (31)$$

(ii.) *Two layers.*—Four electrons in inner, two in outer layer. Atom at $(0, 0, 0)$, electrons at $(\pm a, 0, b)$, $(0, \pm a, -b)$, $(0, 0, \pm d)$. The inner electrons lie at the corners of a tetrahedron, distorted by the two electrons lying on lines joining the atom to the middle points of two non-intersecting edges of the tetrahedron.

$$\begin{aligned} \frac{V}{e^2} = & -6 \left\{ \frac{4}{\sqrt{a^2 + b^2}} - \frac{4c}{2(a^2 + b^2)} \right\} - 6 \left\{ \frac{2}{d} - \frac{2c}{2d^2} \right\} \\ & + 2 \left\{ \frac{1}{2a} + \frac{2}{\sqrt{2a^2 + 4b^2}} \right\} + \frac{1}{2d} + \frac{4}{\sqrt{a^2 + (d-b)^2}} \\ & \quad \quad \quad \frac{4}{\sqrt{a^2 + (d+b)^2}} \quad \dots \quad (32) \end{aligned}$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial d} = 0$ give

$$-\frac{24a}{(a^2+b^2)^{3/2}} + \frac{24ca}{(a^2+b^2)^2} + \frac{1}{a^2} + \frac{8a}{(2a^2+4b^2)^{3/2}} + \frac{4a}{(a^2+(d-b)^2)^{3/2}} + \frac{4a}{(a^2+(d+b)^2)^{3/2}} = 0, \quad (33)$$

$$-\frac{24b}{(a^2+b^2)^{3/2}} + \frac{24cb}{(a^2+b^2)^2} + \frac{16b}{(2a^2+4b^2)^{3/2}} - \frac{4(d-b)}{(a^2+(d-b)^2)^{3/2}} + \frac{4(d+b)}{(a^2+(d+b)^2)^{3/2}} = 0, \quad (34)$$

$$-\frac{23}{2d^2} + \frac{12c}{d^3} + \frac{4(d-b)}{(a^2+(d-b)^2)^{3/2}} + \frac{4(d+b)}{(a^2+(d+b)^2)^{3/2}} = 0. \quad (35)$$

An approximate solution, neglecting a/d and b/d , suggests the trial solution :

$$a = (1+x)c, \quad b = \cdot 6(1+y)c, \quad d = 3\cdot 4(1+z)c.$$

Neglecting squares and higher powers of x , y , and z , equations (33), (34), (35) give

$$\begin{aligned} \cdot 0763 - 2\cdot 5120x - \cdot 8086y - \cdot 1572z &= 0, \\ \cdot 0050 - 1\cdot 0498x - \cdot 7799y - \cdot 5471z &= 0, \\ -\cdot 0089 - \cdot 04622x - \cdot 0223y - \cdot 6141z &= 0. \end{aligned}$$

$$\begin{aligned} \text{Hence} \quad x &= \cdot 04726, & y &= -\cdot 0366, & z &= \cdot 044, \\ \text{and} \quad a &= 1\cdot 047c, & b &= \cdot 5780c, & d &= 3\cdot 55c. \end{aligned}$$

$$\text{Therefore} \quad V = -\frac{e^2}{c} \times 8\cdot 868, \quad (36)$$

and the distances of the electrons from the atom are

$$\left. \begin{aligned} 1\cdot 196c & \text{ (four electrons),} \\ 3\cdot 55c & \text{ (two electrons).} \end{aligned} \right\} \quad (37)$$

VIII. Atom with seven electrons.

$$n=7, E=7e.$$

(i.) *One layer*.—Five electrons at the corners of a regular pentagon, at the centre of which the atom lies, and two at equal distances from the atom on a line through it perpendicular to the pentagon.

Distance of each of the five electrons from the atom = a ,

„ „ „ two „ „ „ = b .

$$V = -7e^2 \left\{ \frac{5}{a} - \frac{5c}{2a^2} + \frac{2}{b} - \frac{2c}{2b^2} \right\} + \frac{10}{\sqrt{a^2 + b^2}} + \frac{1}{2b} \\ + \frac{5}{2} \left\{ \frac{2}{a \cdot 2 \sin 36^\circ} + \frac{2}{a \cdot 2 \sin 72^\circ} \right\} \quad \dots \quad (38)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$ give

$$\frac{28 \cdot 1185}{a^2} - \frac{10a}{(a^2 + b^2)^{3/2}} - \frac{35c}{a^3} = 0, \quad \dots \quad (39)$$

$$\frac{13 \cdot 5}{b^2} - \frac{10b}{(a^2 + b^2)^{3/2}} - \frac{14c}{b^3} = 0. \quad \dots \quad (40)$$

Eliminating c and putting $\frac{a}{b} = x$, we get

$$56 \cdot 237x - 67 \cdot 5 - \frac{10(2x^4 - 5)}{(x^2 + 1)^{3/2}} = 0. \quad \dots \quad (41)$$

Solving graphically, it is found that $x = 1 \cdot 0496$.

$$\text{Hence} \quad \left. \begin{aligned} a &= 1 \cdot 4384c, \\ b &= 1 \cdot 3702c, \end{aligned} \right\} \quad \dots \quad (42)$$

$$\text{and} \quad V = -\frac{e^2}{c} \times 12 \cdot 185. \quad \dots \quad (43)$$

It is seen from (42) that two of the electrons are slightly nearer to the atom than the remaining five.

(ii.) *Two layers.*—Five electrons in inner, two in outer layer. Three of the electrons lie at the corners of an equilateral triangle, the atom at its centroid, and the remaining electrons on a line through the atom perpendicular to the plane of the triangle, and symmetrically disposed with regard to it.

Distance of three electrons from atom = a , } inner layer.
 „ two „ „ „ = b , }
 „ two „ „ „ = d , outer layer.

$$\frac{V}{e^2} = -7 \left\{ \frac{3}{a} + \frac{2}{b} + \frac{2}{d} - \frac{3c}{2a^2} - \frac{2c}{2b^2} - \frac{2c}{2d^2} \right\} + 3 \times \frac{2}{\sqrt{3}a} \\ + \frac{2 \times 3}{\sqrt{a^2 + b^2}} + \frac{2 \times 3}{\sqrt{a^2 + d^2}} + \frac{2}{d-b} + \frac{2}{d+b} + \frac{1}{2b} + \frac{1}{2d}. \quad (44)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial d} = 0$
give

$$\frac{19.268}{a^2} - \frac{6a}{(a^2 + b^2)^{3/2}} - \frac{6a}{(a^2 + d^2)^{3/2}} - \frac{21c}{a^3} = 0, \quad (45)$$

$$\frac{13.5}{b^2} + \frac{2}{(d-b)^2} - \frac{2}{(d+b)^2} - \frac{6b}{(a^2 + b^2)^{3/2}} - \frac{14c}{b^3} = 0, \quad (46)$$

$$\frac{15.5}{d^2} + \frac{2}{(d-b)^2} - \frac{2}{(d+b)^2} - \frac{6d}{(a^2 + d^2)^{3/2}} - \frac{14c}{d^3} = 0. \quad (47)$$

An approximate solution, obtained by neglecting a/d and b/d , suggests the trial solution

$$a = 1.25(1+x)c, \quad b = 1.25(1+y)c, \quad d = 4(1+z)c,$$

where the squares and higher powers of x , y , and z are to be neglected.

Equations (45), (46), (47) give

$$\begin{aligned} & .0313 + 2.1558x + .5434y + .0743z = 0, \\ & .1541 + .8189x + 2.5847y - .3294z = 0, \\ & -.01903 + .0435x - .1029y + .2070z = 0. \end{aligned}$$

Hence $x = -.005, \quad y = -.047, \quad z = .079,$

$$\text{and } \left. \begin{aligned} a &= 1.244c, \\ b &= 1.191c, \\ d &= 4.316c. \end{aligned} \right\} \quad (48)$$

Therefore $V = -\frac{e^2}{c} \times 12.096. \quad (49)$

(iii).—*Two layers.* Six electrons in inner, one in outer layer. A number of arbitrary arrangements were studied, but the equilibrium position was not found on account of the complexity of the equations involved. If the positions of the electrons are given by $[a, 0, 0]$, $[g, \pm b, 0]$, $[g, 0, \pm b]$, $[-d, 0, 0]$, $[f, 0, 0]$, the atom being at the origin, then six of the electrons lie at the corners of an octahedron, and the remaining electron lies on a line joining the atom to one of the corners. This is an equilibrium distribution, but on account of the large number of unknown quantities involved, the solution would be very laborious.

The value of V is given by

$$\begin{aligned} \frac{V}{e^2} = & -7 \left\{ \frac{1}{a} + \frac{1}{d} + \frac{1}{f} + \frac{4}{\sqrt{b^2 + g^2}} - \frac{c}{2} \left(\frac{1}{a^2} + \frac{1}{d^2} + \frac{1}{f^2} \right. \right. \\ & \left. \left. + \frac{4}{b^2 + g^2} \right) \right\} + \frac{1}{f-a} + \frac{1}{f+d} + \frac{4}{\sqrt{(f-g)^2 + b^2}} + \frac{1}{a+d} \\ & + \frac{4}{\sqrt{(a-g)^2 + b^2}} + \frac{4}{\sqrt{(d+g)^2 + b^2}} + \frac{2}{2b} + \frac{4}{\sqrt{2} \cdot b}. \quad (50) \end{aligned}$$

Arbitrary values were assigned to a, b, d, f , and g , as follow:—

$$(A) \quad g=0, \quad a=b=d=1.3119c, \quad f=7c;$$

$$\therefore \quad V = -\frac{e^2}{c} \times 12.257. \quad \dots (51 A)$$

$$(B) \quad g=0, \quad a=b=d=1.3c, \quad f=7c;$$

$$\therefore \quad V = -\frac{e^2}{c} \times 12.2684. \quad \dots (51 B)$$

$$(C) \quad g=0, \quad a=d=1.352c, \quad b=1.267c, \quad f=6.93c;$$

$$\therefore \quad V = -\frac{e^2}{c} \times 12.6611. \quad \dots (51 C)$$

These arbitrary distributions give values of V less than those obtained for the two equilibrium positions studied, and show that those positions are not the most stable ones.

VIII. Atom with eight electrons.

$$n=8, \quad E=8e.$$

(i.) *One layer.*—Electrons at the corners of a cube of edge $2a$, atom at the centre of this cube.

$$\begin{aligned} \frac{V}{e^2} = & -8 \times 8 \left\{ \frac{1}{\sqrt{3}a} - \frac{c}{2 \times 3a^2} \right\} + \frac{8}{2} \left\{ \frac{3}{2a} + \frac{3}{2\sqrt{2} \cdot a} \right. \\ & \left. + \frac{1}{2\sqrt{3}a} \right\}. \quad (52) \end{aligned}$$

The condition of equilibrium $\frac{dV}{da} = 0$ gives

$$\frac{c}{a} = 1.198, \quad a = .8347c.$$

$$\text{Hence} \quad V = -\frac{e^2}{c} \times 15.28. \quad \dots (53)$$

The distance of the electrons from the atom

$$= \sqrt{3}a = 1.446c. \quad \dots (54)$$

(ii.) *One layer.*—Electrons at the corners of a twisted cube, atom at the centre of this figure. The coordinates of the electrons are $(\pm a, \pm a, +b)$, $(0, \pm \sqrt{2}a, -b)$, $(\pm \sqrt{2}a, 0, -b)$, and those of the atom $(0, 0, 0)$.

$$\frac{V}{e^2} = -64 \left\{ \frac{1}{\sqrt{2a^2+b^2}} - \frac{c}{2(2a^2+b^2)} \right\} + \frac{8}{2} \left\{ \frac{2}{2a} + \frac{2}{\sqrt{4a^2+4b^2-2\sqrt{2}\cdot a^2}} + \frac{2}{\sqrt{4a^2+4b^2+2\sqrt{2}\cdot a^2}} + \frac{1}{2\sqrt{2}a} \right\} \quad (55)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$ and $\frac{\partial V}{\partial b} = 0$ give

$$\frac{16 \times 2a}{(2a^2+b^2)^{3/2}} - \frac{8c \cdot 4a}{(2a^2+b^2)^2} - \frac{1.3536}{a^2} - \frac{.2928a}{(.2928a^2+b^2)^{3/2}} - \frac{1.7072a}{(1.7072a^2+b^2)^{3/2}} = 0 \dots \quad (56)$$

$$\frac{16 \times b}{(2a^2+b^2)^{3/2}} - \frac{8c \times 2b}{(2a^2+b^2)^2} - \frac{b}{(.2928a^2+b^2)^{3/2}} - \frac{b}{(1.7072a^2+b^2)^{3/2}} = 0 \dots \quad (57)$$

Eliminating c and putting $x=b/a$,

$$-.6768 + \frac{.8536}{(.2928+x^2)^{3/2}} + \frac{.1464}{(1.7072+x^2)^{3/2}} = 0 \dots \quad (58)$$

A graphical solution of (58) gives $x=.96$.

Hence $b=.8128c$ and $a=.8467c$.

$$\text{and } V = -\frac{e^2}{c} \times 16.75 \dots \quad (59)$$

The distance of an electron from the atom

$$= \sqrt{2a^2+b^2} = 1.447c \dots \quad (60)$$

(iii.) *Two layers.*—Electrons at the corners of two similarly orientated regular tetrahedra. The edges of the tetrahedra are a and b respectively, where $a > b$.

$$\frac{V}{e^2} = 8 \times 4 \left\{ \frac{2\sqrt{2}}{\sqrt{3}a} - \frac{c \cdot 8}{2 \times 3a^2} \right\} - 8 \times 4 \left\{ \frac{2\sqrt{2}}{\sqrt{3}b} - \frac{c \times 8}{2 \times 3b^2} \right\} + \frac{4 \times 3}{2a} + \frac{4 \times 3}{2b} + 4 \left\{ \frac{2\sqrt{2}}{\sqrt{3}(a-b)} + \frac{3 \times 2 \times \sqrt{2}}{\sqrt{3a^2+3b^2+2ab}} \right\} \dots \quad (61)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$ and $\frac{\partial V}{\partial b} = 0$ give

$$\frac{11.57}{a^2} - \frac{64c}{3a^3} - \frac{2\sqrt{2}}{\sqrt{3}(a-b)^2} - \frac{6\sqrt{2}(3a+b)}{(3a^2+3b^2+2ab)^{3/2}} = 0, \quad (62)$$

$$\frac{11.57}{b^2} - \frac{64c}{3b^3} + \frac{2\sqrt{2}}{\sqrt{3}(a-b)^2} - \frac{6\sqrt{2}(3b+a)}{(3a^2+3b^2+2ab)^{3/2}} = 0. \quad (63)$$

Eliminating c and putting $a/b = x$, we get

$$11.57 - \frac{1.633(x^3+1)}{(x-1)^2} - \frac{8.485(x+1)(3x^2+x+3)}{(3x^2+2x+3)^{3/2}} = 0. \quad (64)$$

A graphical solution gives $x = 2.81$.

$$\begin{aligned} \text{Hence } b &= 1.808c, & a &= 5.083c, \\ \text{and } V &= -\frac{e^2}{c} \times 14.73. \end{aligned} \quad (65)$$

The distances of the electrons from the atom are

$$\left. \begin{aligned} 1.105c & \text{ (four electrons),} \\ 3.108c & \text{ (four electrons).} \end{aligned} \right\} \quad (66)$$

(iv.) *Two layers*.—Electrons at corners of two regular tetrahedra, placed so that each face of one is parallel to a face of the other, but on the opposite side of the atom. The distances of the electrons from the atom are a and b .

$$\begin{aligned} \frac{V}{e^2} &= -8 \left\{ \frac{4}{a} - \frac{4c}{2a^2} + \frac{4}{b} - \frac{4c}{2b^2} \right\} + \frac{3}{2} \times \frac{4\sqrt{3}}{2\sqrt{2}a} \\ &+ \frac{3}{2} \times \frac{4\sqrt{3}}{2\sqrt{3}b} \times 4 \left\{ \frac{1}{a+b} + \frac{3}{\sqrt{a^2 - \frac{2}{3}ab + b^2}} \right\} \quad (67) \end{aligned}$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, give

$$\frac{28.326}{a^2} - \frac{32c}{a^3} - \frac{4}{(a+b)^2} - \frac{12(a-b/3)}{(a^2 - \frac{2}{3}ab + b^2)^{3/2}} = 0, \quad (68)$$

$$\frac{28.326}{b^2} - \frac{32c}{b^3} - \frac{4}{(a+b)^2} - \frac{12(-a/3+b)}{(a^2 - \frac{2}{3}ab + b^2)^{3/2}} = 0. \quad (69)$$

Eliminating c and putting $x = b/a$,

$$7.0815 - \frac{(1+x+x^2)}{(1+x)^2} - \frac{(1+x)(3x^2-x+3)}{(1-\frac{2}{3}x+x^2)^{3/2}} = 0. \quad (70)$$

A graphical solution gives $x = .77$.

$$\text{Hence} \quad \left. \begin{aligned} a &= 1.705c, \\ b &= 1.312c, \end{aligned} \right\} \quad \dots \dots \dots (71)$$

$$\text{and} \quad V = -\frac{e^2}{c} \times 14.797. \quad \dots \dots \dots (72)$$

(v.) *Two layers*.—Six electrons in inner layer, two in outer. Coordinates of electrons are $(\pm a, \pm a, 0)$, $(0, 0, \pm b)$, $(0, 0, \pm d)$, and those of the atom $(0, 0, 0)$. Four of the electrons are therefore at the corners of a square, the atom lying at its centre, and the remaining four lie symmetrically on a line through the atom perpendicular to the plane of the square.

$$\begin{aligned} V_{e^2} = & -8 \left\{ \frac{4}{\sqrt{2a}} + \frac{2}{b} + \frac{2}{d} - \left(\frac{c \cdot 4}{2 \times 2a^2} + \frac{2c}{2b^2} + \frac{2c}{2d^2} \right) \right\} \\ & + \frac{4}{2} \left\{ \frac{1}{a} + \frac{1}{2\sqrt{2a}} + \frac{2}{\sqrt{2a^2+b^2}} + \frac{2}{\sqrt{2a^2+d^2}} \right\} + \frac{4}{\sqrt{2a^2+b^2}} \\ & + \frac{1}{d-b} + \frac{1}{d+b} + \frac{1}{2b} + \frac{4}{\sqrt{2a^2+d^2}} + \frac{1}{d-b} + \frac{1}{d+b} + \frac{1}{2d}. \end{aligned} \quad \dots \dots \dots (73)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial d} = 0$, give

$$\frac{19.9232}{a^2} - \frac{16a}{(2a^2+b^2)^{3/2}} - \frac{16a}{(2a^2+d^2)^{3/2}} - \frac{16c}{a^3} = 0, \quad \dots (74)$$

$$\frac{31}{2b^2} + \frac{2}{(d-b)^2} - \frac{2}{(d+b)^2} - \frac{8b}{(2a^2+b^2)^{3/2}} - \frac{16c}{b^3} = 0, \quad \dots (75)$$

$$\frac{31}{2d^2} - \frac{2}{(d-b)^2} - \frac{2}{(d+b)^2} - \frac{8d}{(2a^2+d^2)^{3/2}} - \frac{16c}{d^3} = 0. \quad \dots (76)$$

An approximate solution obtained by neglecting a/d and b/d suggests the trial solution

$$a = .8(1+x)c, \quad b = 1.2(1+y)c, \quad d = 5(1+z)c,$$

where squares and higher powers of x , y , and z are to be neglected.

Equations (74), (75), (76) give approximately

$$\begin{aligned} & -.2301 + 2.7592x + .3540y + .0222z = 0, \\ & -.7304 + 3.0211x + 9.1286y - .2804z = 0, \\ & +.0046 + .0889x - .0673y + .1831z = 0. \end{aligned}$$

$$\text{Hence} \quad x = .08, \quad y = .056, \quad z = -.04,$$

$$\text{and} \quad a = .864c, \quad b = 1.267c, \quad d = 4.80c.$$

Therefore
$$V = -\frac{e^2}{c} \times 16.052. \quad \dots \dots (77)$$

The distances of the electrons from the atoms are

$$\left. \begin{array}{l} 1.221c \text{ (four electrons),} \\ 1.267c \text{ (two electrons),} \\ 4.80c \text{ (two electrons).} \end{array} \right\} \dots \dots (78)$$

A more exact solution of the equations of equilibrium is given by

$$a = .909c, \quad b = 1.267c, \quad d = 4.80c.$$

This gives

$$V = -\frac{e^2}{c} \times 15.01, \quad \dots \dots (77 A)$$

and the distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.287c \text{ (four electrons),} \\ 1.267c \text{ (two electrons),} \\ 4.80c \text{ (two electrons).} \end{array} \right\} \dots \dots (78 A)$$

IX. Atom with twelve electrons.

$$n = 12, E = 12e.$$

(i.) *Two layers.*—Six electrons in each layer. Coordinates of electrons are $(\pm a, 0, 0)$, $(0, \pm a, 0)$, $(0, 0, \pm a)$, $(\pm b, 0, 0)$, $(0, \pm b, 0)$, $(0, 0, \pm b)$, and of the atom $(0, 0, 0)$, where $b > a$.

$$\begin{aligned} \frac{V}{e^2} = & -72 \left\{ \frac{1}{a} - \frac{c}{2a^2} + \frac{1}{b} - \frac{c}{2b^2} \right\} + \frac{6}{2} \left\{ \frac{4}{\sqrt{2}a} + \frac{1}{2a} \right\} \\ & + \frac{6}{2} \left\{ \frac{4}{\sqrt{2}b} + \frac{1}{2b} \right\} + 6 \left\{ \frac{1}{b-a} + \frac{4}{\sqrt{a^2+b^2}} + \frac{1}{a+b} \right\}. \quad (79) \end{aligned}$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, give

$$\frac{24}{a^2} - \frac{24c}{a^3} - \frac{3.3288}{a^2} + \frac{2}{(b-a)^2} - \frac{8a}{(a^2+b^2)^{3/2}} - \frac{2}{(a+b)^2} = 0, \quad \dots \dots (80)$$

$$\frac{24}{b^2} - \frac{24c}{b^3} - \frac{3.3288}{b^2} - \frac{2}{(b-a)^2} - \frac{8b}{(a^2+b^2)^{3/2}} - \frac{2}{(a+b)^2} = 0. \quad \dots \dots (81)$$

Eliminating c and putting $x = b/a$,

$$10.3356 - \frac{(1+x^2)}{(x-1)^3} - \frac{4(1+x)}{(1+x^2)^{3/2}} - \frac{(1+x+x^2)}{(1+x)^2} = 0. \quad (82)$$

A graphical solution gives $x=2.65$.

$$\text{Hence } \left. \begin{array}{l} a=1.148c, \\ b=3.042c, \end{array} \right\} \dots \dots \dots (83)$$

$$\text{and } V = -\frac{e^2}{c} \times 31.1976. \dots \dots \dots (84)$$

(ii.) *Two layers.*—Eight electrons in inner, four in outer layer. The electrons in the inner layer are supposed to lie at the corners of a cube; those in the outer at the corners of a tetrahedron, two edges of which are parallel to two edges of the cube. The coordinates of the electrons are $(\pm a, \pm a, \pm a)$, $(b, b, 2b)$, $(-b, -b, -2b)$, $(-b, +b, -2b)$, $(b, -b, -2b)$, and those of the atom $(0, 0, 0)$. The distortion of the cube on account of the atoms in the outer layer is neglected.

$$\begin{aligned} \frac{V}{e^2} = & -12 \left[8 \left\{ \frac{1}{\sqrt{3}a} - \frac{c}{2 \times 3a^2} \right\} + 4 \left\{ \frac{1}{\sqrt{6}b} - \frac{c}{2 \times 6b^2} \right\} \right] \\ & + \frac{1}{2} \left[8 \left\{ \frac{3}{2a} + \frac{3}{2\sqrt{2}a} + \frac{1}{2\sqrt{3}a} \right\} + 4 \left\{ \frac{1}{2\sqrt{2}b} + \frac{2}{2\sqrt{5}b} \right\} \right] \\ & + 4 \left[\begin{array}{l} \frac{1}{\sqrt{2(b-a)^2 + (2b-a)^2}} + \frac{2}{\sqrt{(b-a)^2 + (b+a)^2 + (2b-a)^2}} \\ \quad + \frac{1}{\sqrt{(b+a)^2 + (2b-a)^2}} \\ + \frac{1}{\sqrt{2(b-a)^2 + (2b+a)^2}} + \frac{2}{\sqrt{(b-a)^2 + (b+a)^2 + (2b+a)^2}} \\ \quad + \frac{1}{\sqrt{2(b+a)^2 + (2b+a)^2}} \end{array} \right] \dots (85) \end{aligned}$$

If we neglect squares and higher powers of a/b , this becomes

$$\begin{aligned} \frac{V}{e^2} = & -12 \left[\frac{8}{\sqrt{3}a} - \frac{8c}{2 \times 3a^2} + \frac{4}{\sqrt{6}b} - \frac{4c}{2 \times 6b^2} \right] \\ & + \frac{11.3976}{a} + \frac{1.6016}{b} + \frac{32}{\sqrt{6}b}. \dots (86) \end{aligned}$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, give

$$\frac{44.0328}{a^2} - \frac{32c}{a^3} = 0, \dots \dots \dots (87)$$

$$\frac{4.9312}{b^2} - \frac{8c}{b^3} = 0. \dots \dots \dots (88)$$

$$\text{Hence } a = .7267c, \quad b = 1.622c,$$

$$\text{and } V = -\frac{e^2}{c} \times 31.808. \dots \dots \dots (89)$$

The distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.258c \text{ (eight electrons), } \\ 3.973c \text{ (four electrons). } \end{array} \right\} \dots \dots (90)$$

X. *Atom with twenty-two electrons.*

$$n=22, E=22e.$$

(i.) *Three layers.*—Eight, eight, and six electrons in the consecutive layers, starting from the inmost. Coordinates of electrons $(\pm a, \pm a, \pm a)$, $(\pm b, \pm b, \pm b)$, $(\pm d, 0, 0)$, $(0, \pm d, 0)$, $(0, 0, \pm d)$, and of atom $(0, 0, 0)$.

$$\begin{aligned} \frac{V}{e^2} = & -22 \left[8 \left\{ \frac{1}{\sqrt{3}a} - \frac{c}{2 \times 3a^2} \right\} + 8 \left\{ \frac{1}{\sqrt{3}b} - \frac{c}{2 \times 3b^2} \right\} \right. \\ & + 6 \left\{ \frac{1}{d} - \frac{c}{2d^2} \right\} \left. \right] + \frac{8}{2} \left\{ \frac{3}{2a} + \frac{3}{2\sqrt{2}a} + \frac{1}{2\sqrt{3}a} \right\} \\ & + \frac{8}{2} \left\{ \frac{3}{2b} + \frac{3}{2\sqrt{2}b} + \frac{1}{2\sqrt{3}b} \right\} + \frac{6}{2} \left\{ \frac{4}{\sqrt{2}d} + \frac{1}{2d} \right\} \\ & + 8 \left\{ \frac{1}{\sqrt{3}(a+b)} + \frac{3}{\sqrt{(a-b)^2 + 2(a+b)^2}} \right. \\ & + \left. \frac{3}{\sqrt{2(a-b)^2 + (a+b)^2}} + \frac{1}{\sqrt{3}(a+b)} \right\} \\ & + 6 \left\{ \frac{4}{\sqrt{(d-a)^2 + 2a^2}} + \frac{4}{\sqrt{(d+a)^2 + 2a^2}} \right\} \\ & + 6 \left\{ \frac{4}{\sqrt{(d-b)^2 + 2b^2}} + \frac{4}{\sqrt{(d+b)^2 + 2b^2}} \right\} \dots \dots (91) \end{aligned}$$

The conditions of equilibrium are $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial d} = 0$.

If in these a/d and b/d are neglected, the following equations are obtained :—

$$\begin{aligned} 90.2244 \frac{1}{a^2} - \frac{176c}{3a^3} + \frac{8}{\sqrt{3}(b-a)^2} - \frac{24(3a-b)}{(3a^2 - 2ab + 3b^2)^{3/2}} \\ - \frac{24(3a+b)}{(3a^2 + 2ab + 3b^2)^{3/2}} - \frac{8}{\sqrt{3}(a+b)^2} = 0, \dots (92) \end{aligned}$$

$$\begin{aligned} 90.2244 \frac{1}{b^2} - \frac{176c}{3b^3} - \frac{8}{\sqrt{3}(b-a)^2} + \frac{24(a-3b)}{(3a^2 - 2ab + 3b^2)^{3/2}} \\ - \frac{24(a+3b)}{(3a^2 + 2ab + 3b^2)^{3/2}} - \frac{8}{\sqrt{3}(a+b)^2} = 0, \dots (93) \end{aligned}$$

$$122.0136 \frac{1}{d^2} - \frac{132c}{d^3} - \frac{96}{d^2} = 0. \dots \dots (94)$$

Eliminating c between (92) and (93), and putting $a/b = x$,

$$90.2244(1-x) - \frac{8}{\sqrt{3}} \frac{(1+x^3)}{(1-x)^2} - \frac{24(3-x+x^3-3x^4)}{(3-2x+3x^2)^{3/2}} \\ - \frac{24(3+x-x^3-3x^4)}{(3+2x+3x^2)^{3/2}} - \frac{8(1-x^3)}{\sqrt{3}(1+x)^2} = 0. \quad (95)$$

A graphical solution gives $x = .515$.

$$\text{Hence } a = .633c, \quad b = 1.23c,$$

and, from (94),

$$d = 5.074c.$$

$$\text{Therefore } V = -\frac{e^2}{c} \times 95.13. \quad (96)$$

The distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.096c \text{ (eight electrons),} \\ 2.13c \text{ (eight electrons),} \\ 5.074c \text{ (six electrons).} \end{array} \right\} \quad (97)$$

(ii.) *Three layers.*—Eight, twelve, and two electrons in consecutive layers, starting from the inmost. Coordinates of electrons are $(\pm a, \pm a, \pm a)$, $(\pm b, \pm b, 0)$, $(\pm b, 0, \pm b)$, $(0, \pm b, \pm b)$, $(\pm d, 0, 0)$. The distortion of the inner layers due to the presence of the two outer electrons is neglected.

$$V_{e^2} = -22 \left[8 \left\{ \frac{1}{\sqrt{3}a} - \frac{c}{2 \times 3a^2} \right\} + 12 \left\{ \frac{1}{\sqrt{2}b} - \frac{c}{2 \times 2b^2} \right\} \right. \\ + 2 \left\{ \frac{1}{d} - \frac{c}{2d^2} \right\} \left. + \frac{8}{2} \left\{ \frac{3}{2a} + \frac{3}{2\sqrt{2}a} + \frac{1}{2\sqrt{3}a} \right\} \right. \\ + \frac{12}{2} \left\{ -\frac{4}{\sqrt{2}b} + \frac{2}{2b} + \frac{4}{\sqrt{6}b} + \frac{1}{2\sqrt{2}b} \right\} + \frac{1}{2} \times \frac{2}{2d} \\ + 12 \left\{ \frac{2}{\sqrt{2}(b-a)^2 + a^2} + \frac{4}{\sqrt{(b-a)^2 + (b+a)^2 + a^2}} \right. \\ + \frac{2}{\sqrt{2}(b+a)^2 + a^2} \left. \right\} + 2 \left\{ \frac{4}{\sqrt{2}a^2 + (d-a)^2} \right. \\ + \frac{4}{\sqrt{2}a^2 + (d+a)^2} \left. \right\} + \left\{ \frac{4}{\sqrt{b^2 + (d-b)^2}} + \frac{4}{\sqrt{2b^2 + d^2}} \right. \\ \left. + \frac{4}{\sqrt{b^2 + (d+b)^2}} \right\}. \quad (98)$$

The conditions of equilibrium, $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial d} = 0$, become, if a/d and b/d are neglected,

$$\frac{90.2244}{a^2} - \frac{176c}{3a^3} - \frac{24(3a-2b)}{(3a^2-4ab+2b^2)^{3/2}} - \frac{48a \times 3}{(3a^2+2b^2)^{3/2}} - \frac{24(3a+2b)}{(3a^2+4ab+2b^2)^{3/2}} = 0, \quad (99)$$

$$\frac{151.8072}{b^2} - \frac{132c}{3b^3} - \frac{24(-2a+2b)}{(3a^2-4ab+2b^2)^{3/2}} - \frac{48b \times 2}{(3a^2+2b^2)^{3/2}} - \frac{24(2a+2b)}{(3a^2+4ab+2b^2)^{3/2}} = 0, \quad (100)$$

$$\frac{43.5}{d^2} - \frac{44c}{d^3} - \frac{40}{d^2} = 0. \quad (101)$$

Eliminating c between (99) and (100), and putting $x = a/b$,

$$50.602 - 67.667x - \frac{(16-16x+36x^3-54x^4)}{(3x^2-4x+2)^{3/2}} - \frac{4(8-27x^4)}{(3x^2+2)^{3/2}} - \frac{(16+16x-36x^3-54x^4)}{(3x^2+4x+2)^{3/2}} = 0. \quad (102)$$

A graphical solution gives two values of x .

$$x = .42 \quad \text{or} \quad .809.$$

From (101), $d = 12.57c$.

$$(A) \quad x = .42.$$

Then $a = .655c$, $b = 1.56c$, $d = 12.57c$,

$$\text{and} \quad V = -\frac{e^2}{c} \times 96.50. \quad (103)$$

The distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.134c \text{ (eight electrons),} \\ 2.206c \text{ (twelve electrons),} \\ 12.57c \text{ (two electrons).} \end{array} \right\} \quad (104)$$

$$(B) \quad x = .809.$$

Then $a = .890c$, $b = 1.10c$, $d = 12.57c$,

$$\text{and} \quad V = -\frac{e^2}{c} \times 92.72. \quad (105)$$

The distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.541c \text{ (eight electrons),} \\ 1.553c \text{ (twelve electrons),} \\ 12.57c \text{ (two electrons).} \end{array} \right\} (106)$$

Hence in this case the two inner layers have degenerated into one. It will be noticed that this model possesses a higher potential energy than either of the two others considered, and is therefore less stable.

Table showing Potential Energy and Size of Atomic Models.

Number <i>n</i> of Electrons.	Number of Layers.	Distances of Electrons from Atom.	Number of Electrons at given distance.	Potential Energy V.
1	1	$c \times 1.0$		$-\frac{e^2}{c} \times .5$
2	1	$c \times 1.143$		$-\frac{e^2}{c} \times 1.531$
3	1	$c \times 1.238$		$-\frac{e^2}{c} \times 2.934$
	2	$c \times 1.087$ $c \times 1.035$ $c \times 3.577$		$-\frac{e^2}{c} \times 2.787$
4	1	$c \times 1.298$		$-\frac{e^2}{c} \times 4.748$
5	1	$c \times 1.342$ $c \times 1.376$	$\frac{3}{2}$	$-\frac{e^2}{c} \times 6.806$
	2	$\times 1.273$ $\times 1.134$ $\times 5.105$	$\frac{3}{1}$ $\frac{1}{1}$	$-\frac{e^2}{c} \times 6.667$
6	1	$c \times 1.385$		$-\frac{e^2}{c} \times 9.40$
	2	$c \times 1.196$ $c \times 3.55$	$\frac{4}{2}$	$-\frac{e^2}{c} \times 8.868$
7	1	$c \times 1.438$ $c \times 1.370$	$\frac{5}{2}$	$-\frac{e^2}{c} \times 12.185$
	2	$c \times 1.244$ $c \times 1.191$ $c \times 4.316$	$\frac{3}{2}$ $\frac{2}{2}$	$-\frac{e^2}{c} \times 12.096$

Table (cont.).

Number <i>n</i> of Electrons.	Number of Layers.	Distances of Electrons from Atom.	Number of Electrons at given distance.	Potential Energy V.
8	1 (cube)	$c \times 1.446$		$-\frac{e^2}{c} \times 15.28$
	1 (twisted cube)	$c \times 1.447$		$-\frac{e^2}{c} \times 16.75$
	2	$c \times 1.105$ $c \times 3.108$	4 4	$-\frac{e^2}{c} \times 14.73$
	2	$c \times 1.312$ $c \times 1.705$	4 4	$-\frac{e^2}{c} \times 14.80$
	2	$c \times 1.287$ $c \times 1.267$ $c \times 4.80$	4 2 2	$-\frac{e^2}{c} \times 15.01$
12	2	$c \times 1.148$ $c \times 3.042$	6 6	$-\frac{e^2}{c} \times 31.2$
	2	$c \times 1.258$ $c \times 3.973$	8 4	$-\frac{e^2}{c} \times 31.8$
22	3	$c \times 1.096$ $c \times 2.13$ $c \times 5.074$	8 8 6	$-\frac{e^2}{c} \times 95.1$
	3	$c \times 1.134$ $c \times 2.206$ $c \times 12.57$	8 12 2	$-\frac{e^2}{c} \times 96.5$
	3	$c \times 1.541$ $c \times 1.553$ $c \times 12.57$	8 12 2	$-\frac{e^2}{c} \times 92.7$

In the case of atoms with twelve and twenty-two electrons respectively, the error in the value of the potential energy may amount to 1 per cent. In the other cases the figures are reliable only to the first place of decimals, except for atoms with one or two electrons, three electrons in one layer, four electrons, six electrons in one layer, and eight electrons at the corners of a cube, for which a more exact result is obtained, with an error of not more than .01.

It is seen from the table of results that, for values of *n* between 1 and 8, the potential energy is in every case less when the electrons lie in one layer than when they lie in two layers. The one-layer form of the atom will therefore

be the more stable. The difference in energy is, however, small in some cases.

Of the distributions considered when $n=12$, that in which the electrons in the layers number 8 and 4 is the more stable.

For the atom with twenty-two electrons, the first two forms possess potential energies so nearly equal that the accuracy of the calculation does not permit us to judge which is the greater. The third form is less stable.

If we consider the most stable form only for each value of n , it is shown by the following table that an empirical law,

$$\frac{V}{n(n+2)} = \text{constant},$$

holds roughly in the cases considered.

n .	$n+2$.	V .	V/n .	$V/n(n+2)$.
1	3	$-.5 \frac{e^2}{c}$	$-.5 \frac{e^2}{c}$	$-.167 \frac{e^2}{c}$
2	4	$-1.531 \frac{e^2}{c}$	$-.765 \frac{e^2}{c}$	$-.191 \frac{e^2}{c}$
3	5	$-2.934 \frac{e^2}{c}$	$-.976 \frac{e^2}{c}$	$-.195 \frac{e^2}{c}$
4	6	$-4.748 \frac{e^2}{c}$	$-1.187 \frac{e^2}{c}$	$-.198 \frac{e^2}{c}$
5	7	$-6.806 \frac{e^2}{c}$	$-1.361 \frac{e^2}{c}$	$-.180 \frac{e^2}{c}$
6	8	$-9.40 \frac{e^2}{c}$	$-1.567 \frac{e^2}{c}$	$-.196 \frac{e^2}{c}$
7	9	$-12.18 \frac{e^2}{c}$	$-1.74 \frac{e^2}{c}$	$-.193 \frac{e^2}{c}$
8	10	$-16.75 \frac{e^2}{c}$	$-2.094 \frac{e^2}{c}$	$-.209 \frac{e^2}{c}$
12	14	$-31.8 \frac{e^2}{c}$	$-2.65 \frac{e^2}{c}$	$-.190 \frac{e^2}{c}$
22	24	$-96 \frac{e^2}{c}$	$-4.36 \frac{e^2}{c}$	$-.181 \frac{e^2}{c}$

If for $n=8$ the form possessing the greatest symmetry, *i. e.* the cube, is taken, the value obtained for $V/n(n+2)$ is $.191e^2/c$.

If the law of force between an atom and an electron is written in the form

$$\text{force} = \text{an attraction of magnitude } \frac{Ne^2}{r^2} - \frac{Ne^2\alpha}{r^3},$$

where N is the atomic weight, then $c = N\alpha/n$.

Consider the distance of the electron from the atom for elements from lithium to neon, as shown in the table of results.

Element.	<i>n</i> .	N.	Distance of Electron from Atom.		
Lithium ...	1	7	$c \times 1.0$	$a \times 7$	$a \times 7$
Beryllium	2	9	$c \times 1.143$	$a \times 5.14$	$a \times 5.14$
Boron	3	11	$c \times 1.238$	$a \times 4.54$	$a \times 4.52$
Carbon	4	12	$c \times 1.298$	$a \times 3.89$	$a \times 3.88$
Nitrogen ...	5	14	$c \times 1.342$	$a \times 3.76$	$a \times 3.78$
Oxygen	6	16	$c \times 1.385$	$a \times 3.69$	$a \times 3.69$
Fluorine ...	7	19	$c \times 1.438$	$a \times 3.90$	$a \times 3.80$
Neon	8	20	$c \times 1.447$	$a \times 3.62$	$a \times 3.63$

The last column shows the values given by Sir J. J. Thomson (Phil. Mag. vol. xli. p. 524, 1921). The discrepancy which occurs in the cases of nitrogen and fluorine is due to the fact that in Sir J. J. Thomson's work the electrons are assumed to be at equal distances from the atom, whereas it is shown by the above calculations that in the equilibrium position this is not the case for these atoms. The value given in the table as the distance of the electrons from the atom is that common to the greatest number of electrons.

XI. *Atom with twenty-seven electrons.*

Some results of a study of an atom with twenty-seven electrons will now be given, but they can be regarded only as a first approximation to the solution.

One of the electrons is supposed to be at a distance from the atom great compared with that of the others, which have coordinates $(\pm a, \pm a, \pm a)$, $(\pm b, 0, 0)$, $(0, \pm b, 0)$, $(0, 0, \pm b)$, $(0, \pm d, \pm d)$, $(\pm d, 0, \pm d)$, $(\pm d, \pm d, 0)$, the atom being at the origin. The electrons are therefore in four layers, the outermost of which contains one electron, while the order of the others, which contain eight, twelve, and six electrons respectively, is not yet determined. The contribution to the potential energy of the system from the single electron in the outermost layer is assumed to be negligibly small.

The potential energy of the system is

$$24e^2 \times \left[-\frac{4.7217}{a} - \frac{6.3339}{b} - \frac{8.0934}{d} + \frac{c}{2} \left\{ \frac{3}{a^2} + \frac{6.75}{b^2} + \frac{6.75}{d^2} \right\} + \frac{1}{\sqrt{3a^2 - 4ad + 2d^2}} + \frac{2}{\sqrt{3a^2 + 2d^2}} + \frac{1}{\sqrt{3a^2 + 4ad + 2d^2}} + \frac{1}{\sqrt{3a^2 - 2ab + b^2}} + \frac{1}{\sqrt{3a^2 + 2ab + b^2}} + \frac{1}{\sqrt{b^2 - 2bd + 2d^2}} + \frac{1}{\sqrt{b^2 + 2d^2}} + \frac{1}{\sqrt{b^2 + 2bd + 2d^2}} \right]$$

The equations necessary for equilibrium derived from this by partial differentiation with respect to a , b , and d do not admit of a solution by the methods used in the earlier part of this paper, for which it is necessary that one of the quantities a , b , or d should be negligibly small compared with one of the others—a condition which is not found to be fulfilled here.

If each layer is considered separately and its equilibrium position and potential energy found, the effect of electrons outside the layer being neglected, while those inside the layer are supposed to act as though they were all at the centre, the results given below are obtained.

Number of electrons in successive layers, proceeding outwards from the atom.			Distances of electrons in successive layers from the atom.			Potential Energy V.
6	12	8	1.066c	1.598c	4.132c	-141.0 $\frac{e^2}{c}$
12	6	8	1.177c	2.025c	4.132c	-142.6 $\frac{e^2}{c}$
6	8	12	1.066c	1.456c	3.037c	-139.9 $\frac{e^2}{c}$
8	6	12	1.10c	1.557c	3.037c	-140.3 $\frac{e^2}{c}$
12	8	6	1.177c	2.154c	5.060c	-142.9 $\frac{e^2}{c}$
8	12	6	1.10c	1.813c	5.060c	-141.8 $\frac{e^2}{c}$

The values obtained for the potential energy are seen to be nearly equal for all arrangements of the layers, so that it is not possible to determine from these results which form is the most stable.

The distance of the electron in the outermost layer is easily shown to be $27c$, and the contribution to the potential energy from it is $-0.18e^2/c$.

If we take the value $-142.9e^2/c$ for V , and divide by $n(n+2)$, i. e. (27×29) , we find $V/n(n+2) = .183e^2/c$, a value in close agreement with those obtained above for other atoms.

My thanks are due to the Department of Scientific and Industrial Research for a grant which rendered it possible to undertake this work, and to Sir J. J. Thomson for many invaluable suggestions during its progress.

C. A Metal Annular-Jet Vacuum Pump. By IVOR BACKHURST, M.Sc., and G. W. C. KAYE, O.B.E., M.A., D.Sc., The National Physical Laboratory.*

THE all-metal mercury-vapour jet-pump described in a previous paper† presents certain difficulties of construction on account of the welded joints; and accordingly a modification has been devised in which these are avoided. This is made of steel, and embodies in its design features characteristic of both the condensation and jet pump.

Description.

Fig. 1, which is drawn to scale, shows the details of the construction. As will be seen, the boiler occupies the lower third of the pump, the upper two thirds being surrounded by a water-jacket. The outer casing of the pump is made from one piece of weldless steel tube. The lower end is closed by a steel cap, which is tightly screwed on, the joint being rendered air-tight by thorough copper and nickel plating. The screwed joint between a second steel cap on the upper end and the connecting tube to the high-vacuum is similarly plated, the cap being sealed to the pump by means of wax or solder. The re-entrant projection of the connecting tube into the pump tends to check the escape of mercury vapour to the high-vacuum system.

On removing the cap, all the inner parts of the pump may

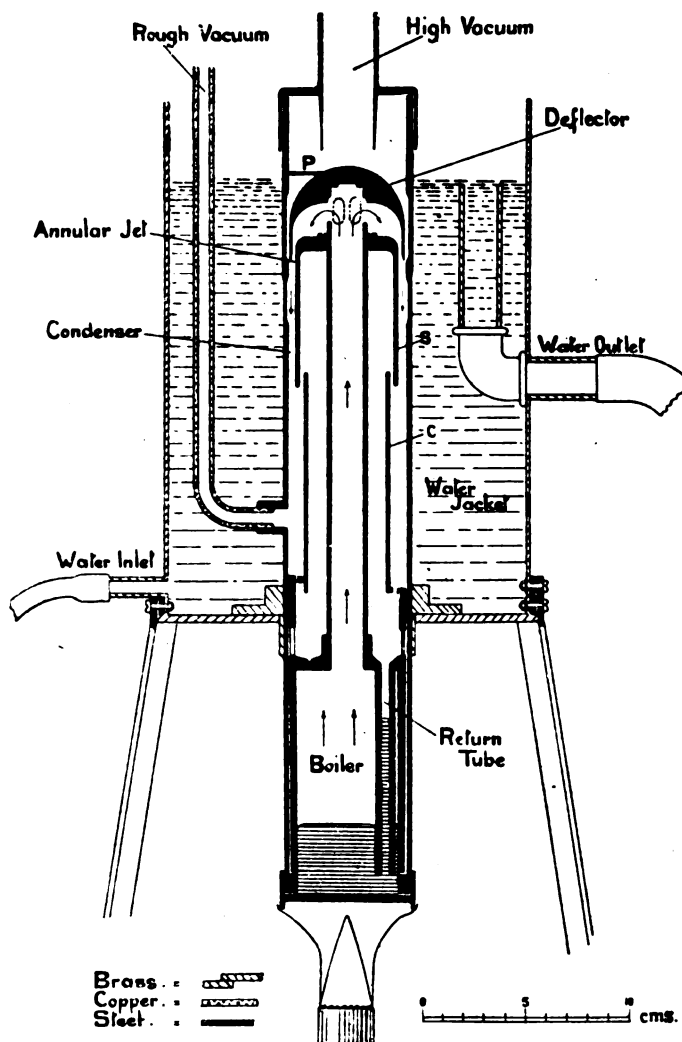
* Communicated by the Director of the National Physical Laboratory.

† Backhurst and Kaye, *supra*, p. 918.

be lifted out together and can then be readily unscrewed apart. This construction makes cleaning exceptionally easy.

Fig. 1.

ANNULAR JET PUMP.



The deflector and sleeve S may be screwed up or down to the positions giving maximum speed over the pressure-range desired. S is fixed by means of a lock-nut (shown) and the

deflector is screwed down on to a washer (shown) of the right thickness to serve as a distance piece. When the deflector is adjusted so that its lower edge is level with the shoulder of the outer casing, the best position is obtained for general work. The curves shown in fig. 2 were obtained with the deflector in this position. Three distance pins, P, screwed into the deflector maintain it concentric with the casing.

The outer casing has two shallow grooves cut on its inner surface, one opposite the deflector, so forming a 'shoulder' for the annular jet, the other just below the jet for the purpose of increasing the efficiency of the water cooling. The amount of mercury required in the boiler is about 700 c.c. (2 lb.).

Action.

The action of the pump is as follows :—Mercury vapour from the boiler passes up the centre tube and through holes at the top to the annular space between the deflector and the sleeve S, from which it issues as a jet and entrains gas diffusing from the annular space between the deflector and the outer casing. In the region between the casing and sleeves S and C, condensation of the vapour takes place, the condensed mercury falling through the hole in C which is immediately above the return tube to the boiler. The sleeve C serves to prevent any mercury vapour which may leak from the boiler through the annular crevice and the several screwed joints just above the boiler from interfering with the vapour jet between S and the outer casing on which the pumping action depends. At the same time it prevents the condensing vapour from this jet from coming in contact with the hot central tube. Since the lower and wider part of C is in contact over an appreciable area with a water-cooled part of the outer casing, and further is separated from the top of the boiler by three pins (shown in fig. 1), it remains comparatively cold, so that the condensed mercury falling on the sloping channelled part of C is not largely re-evaporated, as would happen were it to fall directly on the top of the boiler. It is therefore possible to use a large Bunsen burner and operate the boiler at a comparatively high temperature without any likelihood of failure due to overheating. In this way the blast of vapour obtained is sufficient to supply the annular jet, which has a width of 1.75 mm. and an actual jet area of 2.85 sq. cm. On account of the greater efficiency of the annular jet compared with the circular form, much higher speeds are obtained over the usual jet-pump pressure range. At lower pressures also the pump is still able to operate,

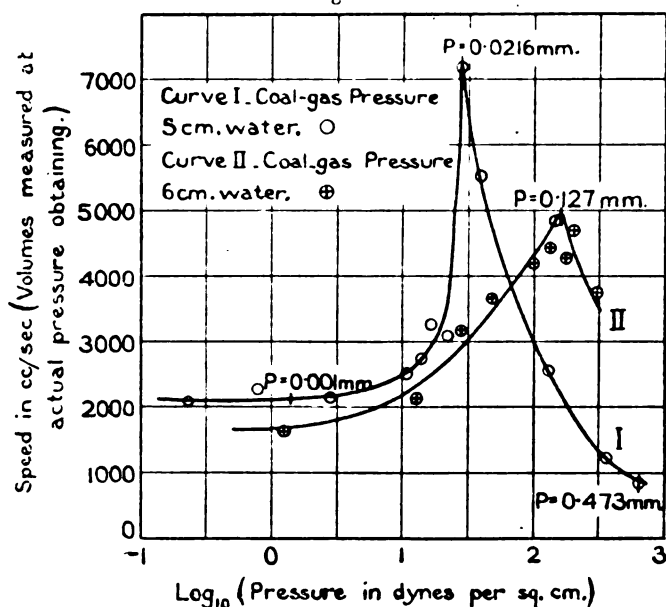
functioning then as a condensation pump, though its speed as such is necessarily restricted by the narrow width of the jet.

The pump could readily be adapted for electrical heating instead of gas.

Speed.

In fig. 2 are curves showing the way in which the speed, as defined by Gaede *, varies with the logarithm of the pressure at which the pump is working. For any particular setting of the annular nozzle the pressure at which maximum

Fig. 2.



speed is obtained depends on the working temperature of the boiler. If this temperature is increased, the maximum in general occurs at a higher pressure. Curves I. and II. were obtained, using a 1-inch diameter Meker burner supplied with gas at pressures of 5 and 6 cm. of water respectively, the general arrangement of the speed-testing apparatus employed being similar to that previously described †. In the present case the dimensions of the flow-tube for the speed tests were:—length 59.0 cm., diameter 1.0095 cm.; and of the tube connecting the latter with the pump, length 18.0 cm.,

* *Suprà*, p. 925.

† *Loc. cit.*

diameter 2.25 cm. Throughout the experiments the supporting vacuum was maintained at 0.9 mm. mercury. The speed values found using another flow tube 38.3 cm. long and 0.5077 cm. in diameter served as a check.

It will be seen from the curves that at pressures between 0.001 and 0.5 mm. mercury the speed varies between 1000 and 7000 c.c./sec., so that the pump is well suited to support a high-speed condensation pump. It is also suitable for maintaining a vacuum in a tube such as a 'gas' X-ray tube, liquid air not being required as the presence of mercury vapour does not interfere with the working of such a tube. When only moderately low pressures are required (as in the 'gas' tube), an adjustable leak of air as by a needle-valve or fine capillary is a convenient means of attaining the desired pressure.

It was found that the pump did not operate to advantage for back pressures exceeding 1 mm. mercury. Under this figure the performance of the pump, both as to speed and vacuum attained, is but little dependent on the back pressure.

Summary.

The mercury-vapour jet-pump of steel, described in a previous paper, presents certain difficulties of construction, and accordingly a modification has been devised which is without welded joints. The pump is similar to the Langmuir type, but has additional inner tubes which together with a narrow annular jet enable it to work against higher back pressures. The pump represents an attempt to combine the advantages of the jet and condensation principles in a single and readily accessible unit. Backed by an ordinary piston oil-pump, it constitutes a complete and efficient high-vacuum outfit. If mercury vapour is an objection, a liquid air trap must be employed. The pump will readily produce a vacuum of the order 0.00001 mm. mercury or less when working against a back pressure of 1 mm. mercury. The speed is high, the actual value, which varies between 1000 and 7000 c.c./sec., depending on the pressure in the vessel being exhausted, and also on the value of the back pressure against which the pump is working.

We wish to acknowledge the assistance given by Mr. J. Balmanno and Mr. W. H. Sewell, of the Observer Staff of the Laboratory.

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CI. *The Electronic Theory of Valency*.—Part IV. *The Origin of Acidity*. By Prof. T. MARTIN LOWRY, C.B.E., M.A., D.Sc., F.R.S.*

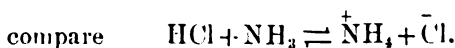
THE object of this communication is to unite into one definite hypothesis a number of suggestions which have been made in earlier papers of this series, and elsewhere, as to the nature of acids and the origin of acidity.

1. *The Nature of Acids.*

An acid may be defined as a *hydride from which a proton can be detached*, e.g. on dissolution in an ionizing solvent, on electrolysis, or by displacement by a metallic ion. This definition † appears likely to hold its own, in spite of proposals that would either restrict its scope ‡, by limiting it to the hydrates of anhydro-acids §, or broaden it to include compounds not containing any hydrogen ||. Thus, although it is true that water is needed to make hydrogen chloride conduct, this does not prove that water is a necessary constituent of an acid, since it may only mean that the proton always seeks out an alternative resting-place when it is threatened with eviction from an acid, and that, if alternative accommodation is not provided, it may refuse to be displaced. In other words, the ionization of an acid may be, not a dissociation as expressed in such an equation as



but a double decomposition of the type



There is therefore no need to narrow the definition of an acid by confining it to compounds which contain oxygen as well as hydrogen. On the other hand, there are real advantages in maintaining the positive relationship between acidity

* Communicated by the Faraday Society.

† Compare *Chemistry and Industry*, xlii. p. 43 (1923).

‡ *Ibid.* p. 46.

§ Werner, 'New Ideas,' 1911, p. 212; compare *Chemistry and Industry*, xlii. p. 1048 (1923).

|| G. N. Lewis, 'Valence,' 1923, p. 142.

and the presence of a proton which is indicated in the definition set out above, in place of widening this definition so as to include any substance which can make away with a hydroxyl ion, or even with another anion, such as a fluoride ion.

2. *The Development of Acidity.*

When the hydrides of the lighter elements are compared, a very remarkable contrast is observed between successive members of a series such as CH_4 , NH_3 , OH_2 , FH , Ne . Thus the monohydrides FH , ClH , BrH , IH are amongst the strongest acids; but SH_2 is already a very weak acid and OH_2 is commonly regarded as neutral. Ammonia is more of a base than an acid, since it is more ready to take up a proton as in NH_4^+Cl^- than to lose one as in NaNH_2^+ . In methane, acidic and basic properties have both disappeared, the former on account of the greater stability of this hydride as compared with NH_3 or OH_2 , the latter on account of the fact that the octet of carbon cannot carry any more radicles beyond the four hydrogen atoms which are already attached to it in methane. In the first paper of this series* I suggested that this progressive disappearance of acidity was not due directly to change of valency, but that it might be associated much more closely with the growing size of the molecule which had been demonstrated by the experiments of Rankine† on the collision-areas of these molecules as deduced from measurements of the viscosity of the gases. This suggestion is repeated in a more precise form in the following paragraph.

3. *Bohr's Atom in Relation to the Problem of Acidity.*

Although the brilliant investigations of Bohr have led at present only to a theory of the structure of free atoms and ions, it is already possible to surmise the direction in which developments must take place in order that it may provide in due course a working hypothesis of the structure of molecules also. In particular, the view is now widely accepted that the "shared electrons" of the static models must be translated into "shared orbits"‡ in the dynamic model of the

* Trans. Faraday Soc. xviii. p. 292 (1923); Phil. Mag. xlv. p. 1116 (1923).

† Trans. Faraday Soc. xvii. p. 719 (1922).

‡ Niessen, Dissertation, Utrecht, 1922; Pauli, *Ann. d. Physik*, lxviii. p. 177 (1922); Campbell, *Nature*, cxi. (Apr. 28, 1923); Fowler, Trans. Faraday Soc. xix. p. 461 (1923); Sidgwick, *ibid.* p. 469.

molecule. In the recent discussion on "The Electronic Theory of Valency" I suggested * that the development of looped orbits may be related in a very simple manner to the well-known relativity effect. In a free atom or ion this gives rise to precession of the orbit; but the intersection of the inward and outward paths, which is the main feature of this effect, is exactly what is needed in order to produce a figure-of-eight orbit enveloping two nuclei. Since the major axis of an orbit is inversely proportional to the effective nuclear charge, it is clear that the size of the loop must be smaller in FH with a nuclear charge of 9 than in CH₄ with a nuclear charge of 6, in complete qualitative agreement with the observations of Rankine. It is not easy to say what relationship will exist between the size of the looped orbit and the magnitude of the force with which it binds together the two nuclei which it encloses; but the repulsion between them must certainly increase rapidly as the two nuclei are brought more closely together by the contraction of the loop. From this point of view it appears that the four hydrogens of methane may be held securely by looped orbits, with the focus of the outer loops at a considerable distance from the nucleus; whereas the much smaller loop in which the proton of hydrogen fluoride is held must bring it nearer to the nucleus, and may easily bring it so near that it can be driven outside the loop by the strong repulsion to which it is subjected.

4. Transmission of Acidity.

It is of interest to reconsider, in the light of the views set out in the preceding paragraph, the mechanism by which acidity is propagated in a chain of atoms, *e.g.* from Cl to H in Cl.CH₂.CO.OH. When a static model is used, the simplest mechanism is that suggested by Langmuir †, namely a displacement of the nuclei relatively to the enveloping shells of electrons. When a dynamic model is used, this conception becomes of less utility, since it is difficult to imagine that the orbits can be diverted very much from their normal course round the nucleus—at any rate in the inner portion of the path. It is therefore more reasonable to suppose that, since an orbit with a chlorine-nucleus in one focus is necessarily of smaller dimensions than a corresponding orbit containing a carbon nucleus, the dimensions of a looped orbit which contains chlorine in one focus and carbon in the other will

* Trans. Faraday Soc. xix. p. 480 (1923).

† Trans. Faraday Soc. xvii. p. 609 (1922).

be intermediate in size between those of binuclear orbits containing either two chlorine or two carbon atoms. It is moreover reasonable to think that the contracted orbits of a chlorine atom may tend to impose a like contraction on orbits of similar quantum-number in an adjacent carbon atom when some of these orbits are shared by both atoms. This effect, transmitted in a diminished degree as the length of the chain is increased, would account for the "general effect" of acylous and basylous radicles, as illustrated by the tables in Part III. of this series of papers.

It will be noticed that this effect is always in the same direction. It has been suggested that, in the transmission of acidity through a chain of atoms, an alternating effect (basylous, acylous, basylous, acylous, etc.) is sometimes produced in consecutive atoms; but, as I have already stated, I am not yet convinced that there is any sufficient experimental basis for this view.

5. Summary and Conclusions.

(a) The increasing acidity of the hydrides from CH_4 to FH or from SiH_4 to ClH is attributed to a progressive diminution in the size of the orbits of the electrons by which the protons are linked to the central nucleus.

(b) It is suggested that acylous atoms such as chlorine tend to diminish the size of the orbits of electrons which they share with another atom, and that this effect can be transmitted to other orbits of the same quantum-number in the latter atom. In this way the transmission of acidity through a chain of atoms can be interpreted by means of a dynamic, instead of a static, model. Conversely, basylous groups must expand the orbits of electrons which they share with other atoms.

(c) From this point of view an unsubstituted hydrocarbon chain should act as a neutral radicle in carboxylic acids, since orbits shared by two carbon atoms will be of normal dimensions. Hydrogen directly attached to an atom of sulphur, phosphorus, etc., is more acylous than an alkyl radicle because it allows for a greater contraction of the orbits; but even a proton is less acylous than the "lone pairs" of electrons in acids such as FH and ClH , since contraction is probably at a maximum in orbits which are entirely unshared.

CII. *On the Emission of Positive Ions from Hot Tungsten.*
 By Professor W. A. JENKINS, *University of Dacca,*
India *.

DURING an investigation upon the alteration of resistance of a tungsten spiral when emitting electrons, it was observed that when the temperature of the spiral reached a certain value a further increase in the temperature resulted in a decrease of the electron current. It has been known for some time that there is a maximum to the current available with a fixed voltage, and that beyond a certain point an increase of temperature does not result in an increase of the electron current. This phenomenon has generally been attributed to the existence of space-charge; but while it is possible to explain the existence of a saturation value by means of the space-charge hypothesis, it does not seem easy on this theory to account for a decrease of the current. More detailed experiments upon the magnitude of the electron current at a high temperature showed that the phenomenon of a decrease of the electron current with increase of temperature was not reproducible with all the tungsten wires used. These experiments, in which a more sensitive galvanometer than usual was employed, revealed the fact that at about the temperature at which the electron current reached a maximum value or commenced to decrease, an emission of positive ions began. This positive current could be observed, of course, by reversing the potential used for the observation of the electron current. The present paper is an account of investigations carried out upon this positive ion emission at high temperatures.

It has long been known that in the presence of gas most metals emit positive ions at fairly low temperatures; but this phenomenon is one which varies enormously under different conditions and which disappears with the elimination of the gas. When a metal is heated in vacuo, and the temperature is not allowed to vary, the emission of positive ions which is great at first gradually diminishes until it is too small to measure. After continued heating in a vacuum, a metal ceases to emit positive ions, but its power may be restored by treating it in one of several ways †.

In addition to this effect, characteristic of new wires heated in a vacuum, it is found that the introduction of almost any gas will cause the production of both positive and negative ions.

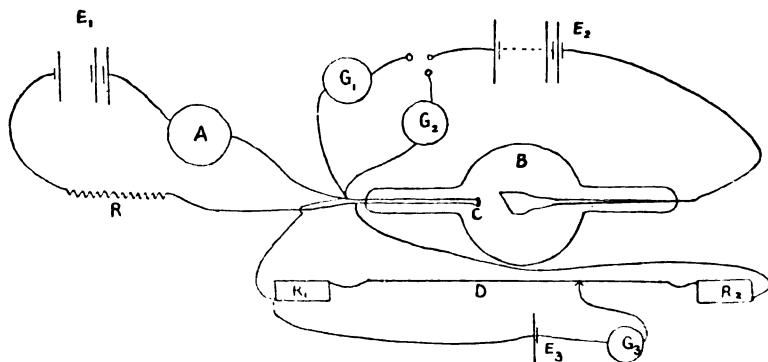
* Communicated by the Author.

† Richardson, 'Emission of Electricity from Hot Bodies,' pp. 202-204.
Phil. Mag. S. 6. Vol. 47. No. 281. May 1924. 3 U

These ions are heavy and are not affected by weak magnetic fields. Richardson and Chaudhuri* have shown that the use of a magnetic field when the driving voltage is small can be used as a criterion of the absence of gas and the formation of ions by collision. According to their experiments a tube can be regarded as satisfactory, *i.e.* free from gas and the wire sufficiently glowing out, when a transverse magnetic field will entirely prevent the electron current from passing between electrodes 2 cm. apart with a driving potential of several volts. In any tube in which there are traces of residual gas, or in which the wire retains traces of occluded gas, the application of a magnetic field will not entirely prevent the electron current from passing. This residual current is attributed to the formation of ions by collision. The positive emissions discussed in the present paper are of an entirely different character, however, from those which have been previously observed.

Apparatus used.

Fig. 1.



E_1 is a battery of twelve 2-volt accumulators used for heating the tungsten spiral in the Coolidge tube B. The current through the tungsten spiral was measured by the ammeter A, and could be varied through wide limits by means of the resistance R.

E_2 is a battery which varied in different parts of the experiment from 2 volts to 220 volts.

G_1 is a galvanometer used for measuring the positive electron current.

* Phil. Mag. Feb. 1923, p. 337.

G_2 is a high sensitivity galvanometer used for measuring the positive emission current.

E_3 is a 2-volt accumulator used in combination with the galvanometer G_3 , the resistances R_1 and R_2 , and the potentiometer wire D for accurately measuring the drop in potential between the terminals of the tungsten spiral. It was found that the ordinary connexions of the Coolidge tube were not sufficiently good to allow of a balancing point on the potentiometer being obtained. Thick copper leads were therefore soldered to the terminals of the spiral after the ordinary connecting cap had been removed. This considerably improved the steadiness of the current through the spiral, and enabled the potential fall between the terminals to be accurately determined.

The Coolidge tube was placed between the poles of a powerful electromagnet, so that the space between the cathode and the anticathode was in the central part of the field. The pole-pieces were, of course, widely separated, but with a current of about $5\frac{1}{2}$ amperes a field of approximately 400 was obtained.

A Coolidge tube is not an ideal form of apparatus for the experiments in question, but for preliminary work it offers many advantages. The vacuum is very high and the spiral is thoroughly glowed out, so that although the tubes used had been employed for X-ray work for several months, a discharge could not be passed through them when the tungsten spiral was cold. The application of the tests employed by Richardson and Chaudhuri for the absence of gas, either residual or occluded, also showed that the tubes were in a satisfactory condition for the experiments. Below a temperature of about 2500°C . there were no positive ions present in the tubes. Further, when a magnetic field of strength 400 was applied at right angles to an electron current flowing under a driving potential of less than 10 volts, the electron current was entirely stopped, even when the current flowing was as high as 3×10^{-4} ampere, the temperature over 3000°C ., and a galvanometer of sensitivity 4×10^{-10} employed.

If voltages greater than 10 were employed, the magnetic field was insufficiently strong to prevent completely the electron current from passing between the electrodes. This is what one would expect, for the velocity of the electrons increases with the driving potential. Whatever effects are observed, therefore, may be presumed to be pure emission effects, unaffected either by the presence of gas within the tube or occluded gas within the spiral.

General Description of the Phenomena observed.

The tungsten spiral was heated in the ordinary manner, and the current gradually increased. At first the discharge was a pure electron discharge following the curve already investigated by many physicists. When the current through the spiral reached a certain value, however, the electron current ceased to increase, and a further increase of the heating current generally resulted in a slight diminution of the electron current. Up to just below this point no positive emission could be detected, even with an applied voltage of over 200 and a very sensitive galvanometer. Further increase of the heating current gave rise to a positive emission, which increased rapidly with the temperature. This positive emission current also varied with the applied voltage—with time—with the previous treatment of the spiral and with the application of a magnetic field. These variations are not simple, and will be described in detail. In order to obtain accurate measurements of this positive emission current, which was generally very small, it was necessary to eliminate all leakage currents. With 24 volts on the heating circuit, 200 volts on the positive emission circuit, and a different 200 volts on the electromagnet circuit some trouble was experienced with insulation. This was eventually overcome by using nothing but air wires (except for the electromagnet) and by placing each individual piece of apparatus upon separate blocks of paraffin-wax. In addition, it was found necessary to place the cells used upon separate tables, and to stand these tables upon blocks of either ebonite or paraffin-wax. Even with these precautions it was not possible to obtain satisfactory readings immediately after a shower of rain when the atmosphere was moist. During the rainy season in Bengal, experiments of this kind are out of the question.

Variation of the Emission with the Temperature.

Keeping the applied voltage constant, experiments were carried out with different tubes, and the results set forth in Table I. obtained. The voltage used was 220, this being the maximum available. In all cases the values shown are the maximum ones obtained neglecting the initial discharge, which will be dealt with later in the paper. The temperatures were not measured directly, but were deduced from the values of the resistance obtained from the current and the potential determinations. For this purpose the data given in Langmuir's paper were used.

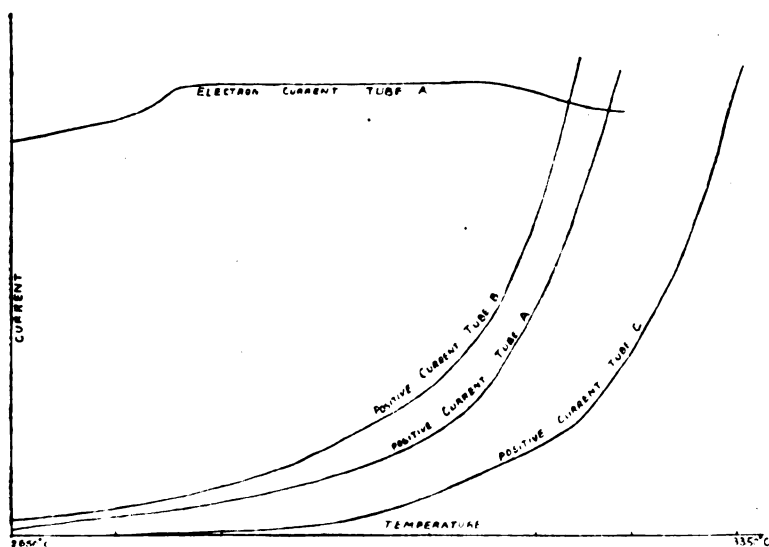
* Langmuir, Physical Review, vi. (1915).

Table I. shows a complete set of data for experiments carried out with the first tube. The results obtained with

TABLE I.

Heating Current.	Resistance (spiral).	Temperature.	Electron Current.	Positive Current.
5.85 amperes.	2.410	3500° C.	79×10^{-5} amp.	370×10^{-7} amp.
5.4 "	2.226	3270	81 "	100 "
5.3 "	2.186	3210	82 "	63 "
5.2 "	2.144	3160	87 "	39 "
5.1 "	2.095	3100	87 "	23 "
5.0 "	2.049	3040	87 "	16 "
4.85 "	1.947	2920	87.5 "	9 "
4.75 "	1.904	2870	87.5 "	6 "
4.65 "	1.872	2830	87 "	6 "
4.55 "	1.843	2790	82 "	4.8 "
4.45 "	1.810	2750	79.5 "	4.8 "
4.35 "	1.777	2710	78.5 "	3.6 "
4.25 "	1.744	2670	77 "	2.4 "
4.15 "	1.711	2620	76 "	2.4 "
4.05 "	1.672	2580	75 "	1.2 "
3.95 "	1.640	2540	74 "	0 "
3.85 "	1.616	2520	72 "	0 "
3.6 "	1.521	2400	66 "	0 "

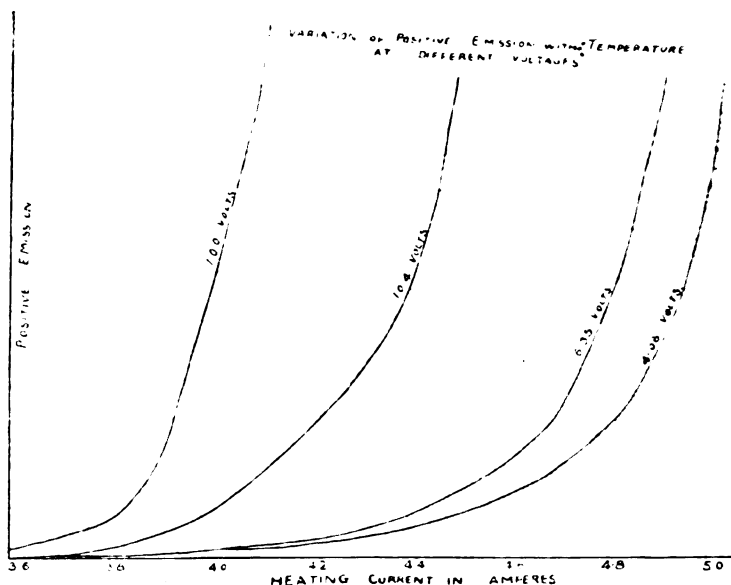
Fig. 2.



other tubes were similar, and are shown in graph form in fig. 2.

It will be observed that the positive currents obtained with the third tube used, *i. e.* tube C, are much smaller than those obtained with the other two tubes. This tube also gave much smaller electron currents than did either of the other two. That the positive discharge does not begin with tube C until a temperature of nearly 2800 C. has been reached is probably due to the fact that below this temperature the emission was so small that the galvanometer used was not capable of detecting it. The scale used for plotting the electron current is, of course, a different one from that used for plotting the positive current. The curves are of similar shape, as is shown

Fig. 3.



in fig. 3, but the magnitudes less when driving voltages of less than 220 volts are used. In the case of these latter voltages, however, the values of the positive emission obtained when a magnetic field is applied must be used in order to get the true emission effect. The reason for this will be discussed later.

It is unlikely that in a Coolidge tube the whole of the emitted particles, whether electrons or positively-charged particles, reach the anticathode, especially when the voltage is small. The conformation of the tube prohibits this, and it is therefore not possible to deduce from the above results

any definite relationship that may exist between the temperature and the positive emission. All that it is possible to say is that as the temperature increases from $2500^{\circ}\text{C}.$ to the melting-point, the emission increases very rapidly. The largest positive emission observed was 5.9×10^{-6} ampere. This was obtained with the first tube, which also gave the greatest currents, and showed no maximum electron emission even with the highest temperatures used. With more suitable forms of tubes in which the emitting wire is entirely surrounded by a receiving electrode, it should be possible to obtain saturation values of the emission current at voltages much less than 220. Such values would enable one to deduce the relation between the temperature and the positive emission. It is proposed to continue the investigations upon these lines.

Variation of the Emission with the Driving Voltage.

Table II. and fig. 4 show the characteristic features of the variation of the emission with the applied voltage up to a maximum of 220 volts. It will be seen that the emission rises uniformly with the voltage up to 16 volts, and then apparently approaches a saturation value. On further increasing the voltage the emission very considerably increases. It is possible that at the higher voltages the potential assists in pulling out the positive particles as well as increasing the velocity. This point also can be more satisfactorily decided in an apparatus in which the whole of the emitted particles are collected on the receiving electrode. For purposes of comparison the variation of the electron current with the applied voltage is also shown.

The results indicate that the electron current increases uniformly with the voltage, and this suggests that the lack of uniformity which marks the variation of the positive current with the voltage is a general phenomenon, and is not due to the asymmetrical shape of the Coolidge tube. If this is so, it is clear that there is some cause operating at the higher voltages which is not present at the lower ones. The table shown is one of many that were obtained using different values of the heating current.

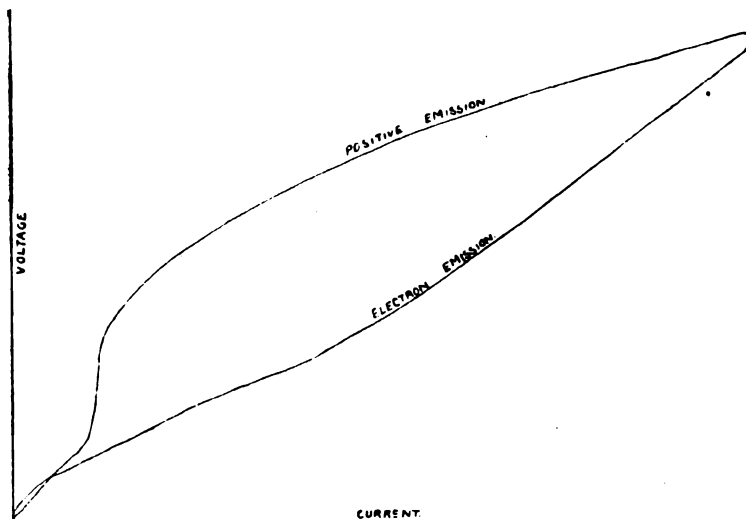
Variation of the Emission with the Magnetic Field.

Table III. shows the values of the electron current obtained for different values of the heating current when different driving voltages were used and a magnetic field of

TABLE II.

Heating Current.	Voltage.	Electron Emission.	Positive Emission.
4.6 amperes.	0	63×10^{-8}	0
	2.08	19×10^{-6}	24×10^{-10}
	4.25	80 "	56 "
	5.84	130 "	80 "
	7.95	227 "	104 "
	10.06	320 "	132 "
	12.16	458 "	169 "
	14.28	528 "	192 "
	16	662 "	212 "
	20	732 "	224 "
	28	1308 "	232 "
	34	1580 "	240 "
	50	2200 "	400 "
	100	3840 "	2080 "
	220	12660 "	5400 "

Fig. 4.



strength 400 Gauss was applied. In conformity with the results of Richardson and Chaudhuri, if the applied voltage be less than 10, the magnetic field entirely destroys the electron current; but if the heating current be large, i.e. if the temperature of the wire be high, then the application of a magnetic field not only destroys the electron current, but

it results in the appearance of a small current flowing in the opposite direction. There appear to be two possible sources for this current. It may either be an electron current flowing from the anticathode to the cathode, or it may be a positive emission current flowing from the heated spiral to the anticathode. The former would be of the nature of a photoelectric current caused by the incidence of ultra-violet light upon the tungsten anticathode. This cannot be ruled out at once as an impossibility, for it must be remembered that the spiral is at a very high temperature and is emitting intense light, and, further, that the vacuum in the tube is extremely high. The latter condition would permit of very short waves reaching the anticathode before being absorbed.

TABLE III.

Current.	2.06 Volts.	4.06 Volts.	6.35 Volts.	8.45 Volts.	10.4 Volts.	25 Volts.	50 Volts.
3.8.....	0	0	0	0	0	6 L	84 L
4.1.....	0	0	0	0	0	36 L	135 L
4.4.....	3 R	0	0	0	0	480 L	720 L
4.65....	13 R	0	0	0	160 L	560 L	1120 L
4.8.....	22 R	1 R	0	0	175 L	600 L	1440 L
5.0.....	38 R	5 R	0	0	180 L	720 L	1752 L
5.1.....	...	...	...	...	...	824 L	2184 L
5.2.....	...	11 R	1 R	0			
5.4.....	...	20 R	3 R	0			

It is not probable, however, that the velocity of electrons emitted as a result of photoelectric action would be sufficiently high to allow of the electrons reaching the heated spiral against the applied potential, and in spite of the magnetic field. Moreover, experiments show that at higher temperatures there is a definite positive emission when the applied voltage is such as to aid in their emission. It seems unnecessary, therefore, to bring in any other hypothesis to account for the phenomena in question than that the current is due to positive charges emitted from the heated spiral and possessing sufficient velocity to overcome small negative potentials, tending to keep them within the heated spiral. The variation of the magnitude of this small positive current

with the temperature of the wire and the applied potential bears out this view. The current is greatest with the highest temperature and the smallest voltage, decreases rapidly as the voltage increases, and becomes zero at even the highest temperature when the applied voltage is 8. This means that the velocity of the positively-charged particles, which are otherwise free to come out, is too small to overcome a restraining potential of 8 volts.

With an applied voltage of 2.06 volts the electron current is entirely stopped even at very high temperatures, and the positive ions overcome the adverse potential of 2.06 volts without difficulty. At 4.06 volts two causes may operate or partially prevent the positive ions from manifesting themselves. In the first place, the potential of 4.96 volts may be sufficient to stop some of them getting across, and secondly, at the higher temperature some of the electrons may possess sufficient velocity to get across in spite of the magnetic field. The former is the more likely reason, for when an applied voltage of 8.45 is used there is no current at all when the magnetic field is put on. It is extremely unlikely that at all the higher temperatures the residual electron current and the positive current will exactly counterbalance each other; so that one must infer that with this applied voltage the electrons have still insufficient velocity to get across when the magnetic field is applied, while the voltage is high enough to prevent all the positive ions from getting across. At higher potentials, as the table shows, some of the electrons get across in spite of the magnetic field.

The R denotes that the deflexions were to the right and a positive current was flowing. L denotes that an electron current was flowing. Table IV. shows the variation of the positive emission with a magnetic field under different conditions. The results as regards magnitude of emission are not absolutely consistent, probably owing to the experiments having been carried out on different days. It is not easy to reproduce exactly any given condition of the tube, and it is by no means certain that exactly the same results would be obtained at different times, even if the conditions were exactly reproduced. The essential features of the phenomena were, however, always reproduced, and considering the nature of the experiments, the results are as consistent as could be expected. When the applied potential was low, the positive emission current increased considerably with the application of the magnetic field. This means that a certain number of electrons were able to reach the anticathode in spite of the adverse potential. The positive emission appeared to be smaller, therefore, than it really was. On switching on the

magnetic field, these electrons were deviated under the joint influence of the magnetic field and the applied potential, and the full positive emission was observed. This increase is more noticeable with the smaller applied voltages than with the large ones, as one would expect. With the highest voltages used, the effect disappeared altogether at the lower temperatures; but at the higher temperatures the reverse effect appeared, *i. e.* the positive emission current showed an unmistakable decrease when the magnetic field was applied. This means that some of the particles carrying charges were either sufficiently light or moved sufficiently slowly to be affected by a field of 400 gauss.

TABLE IV.

Variation of Positive Emission with Magnetic Field.

Current.	2.06 Volts.		4.06 Volts.		6.35 Volts.		8.45 Volts.		10.4 Volts.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
3.5	0	0	0	0	0	0	0	0	0	0
3.75	0	0	0	0	0	1	0	2	0	2
4.0	1	10	2	9	3	4.5	5	13	18	22
4.25	4	16	5	18	10	24	16	29	61	156
4.5	6	40	13	41	23	50	28	54	250	300
4.75	20	114	46	111	145	202	80	140	1140	1710
5.0	86	220	213	453	520	843	175	804	3060	3390
5.1	...	...	...	...	...	780	315	600	...	...
5.25	...	...	630	1200	...	...	690	1200	...	...

Current.	25 Volts.		50 Volts.		100 Volts.		220 Volts.	
	A.	B.	A.	B.	A.	B.	A.	B.
3.5	0	0	0	0	8	8	30	30
3.75	0	2	0	1.5	29	29	55	55
4.0	7	13	6	10	50	50	360	300
4.25	45	57	62	70	1050	840	740	660
4.5	255	260	267	280	3300	2760	2400	2050
4.75	1270	1170	2070	2120	6240	5250	4200	3810
5.0	3090	2550	3660	3840	7200	6840	...	...
5.1	6300	4630	5700	5850	...	...	16500	14400
5.25	...	...	...	...	...	...	...	...

The figures under column A indicate deflexions obtained when no magnetic field was applied. Those under B indicate deflexions obtained when the magnetic field was applied.

There is no evidence as yet of the existence of positive electrons of mass comparable with that of the negative electrons, and one must therefore conclude that some of the positively-charged particles moved with velocities considerably less than those of the negative electrons. The velocity of the emitted positive particles will, of course, increase with the applied potential, and one would expect the effect of the magnetic field to be greater when the lower voltages are used. Any effect of this kind, however, is completely masked at the lower voltages by the fact that negative electrons are able to flow across against the applied potential. It is possible also that when higher voltages are applied, positively-charged particles are torn from the cathode, and that these particles move with a much lower velocity than those which are spontaneously emitted. Fig. 3, showing the variation of emission with voltage, suggests such an effect.

Variation of the Initial Emission with the Previous Treatment of the Spiral.

During the course of the experiments it became apparent that the magnitude of the initial deflexion obtained at any given temperature and applied voltage varied according to the previous treatment of the spiral. If the positive potential were applied before the spiral was heated, then, on heating the spiral, the deflexion remained at zero for some time, depending on the temperature of the spiral, and then gradually rose to its normal value. This was not due to the spiral's requiring a considerable period for attaining its final temperature, for similar experiments with the electron current indicated that the final temperature was quickly attained. Fig. 5 illustrates this phenomenon.

It will be seen that, while the electron current has attained 96 per cent. of its final value 15 seconds after the commencement of the heating and its maximum value after one minute, the positive emission does not begin until after 30 seconds have elapsed, and it does not attain its maximum value until the potential has been applied for approximately 3 minutes. As indicated in fig. 6, this period is longer when the applied voltage is small, but even with an applied voltage of 220 there is no emission during the first 30 seconds. In a Coolidge tube the application of a positive potential of 220 volts would not entirely prevent the emission of electrons, but it would very considerably diminish the outflow.

Fig. 5

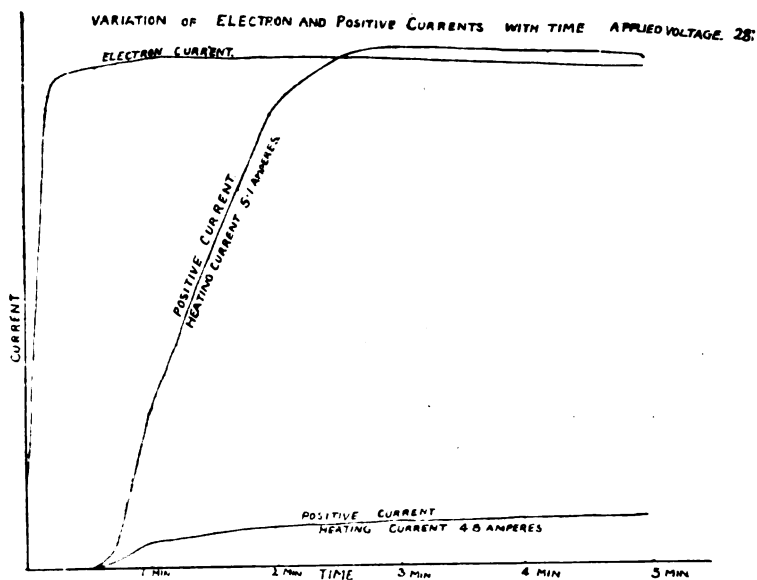
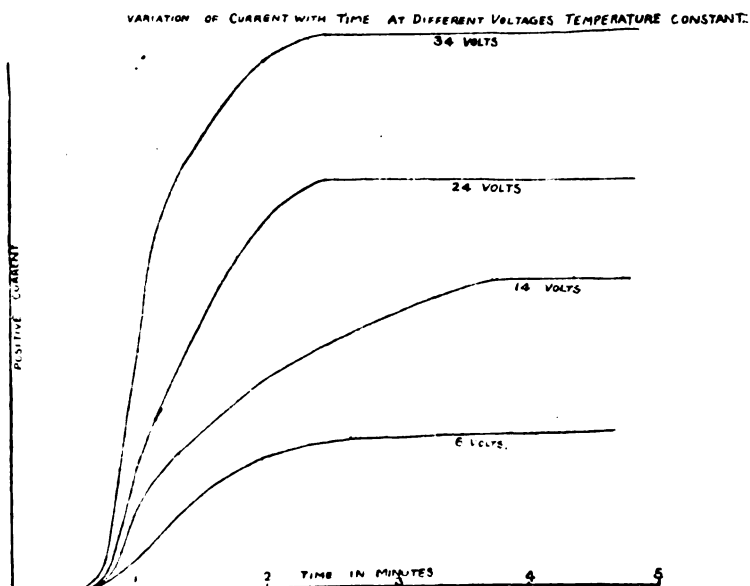


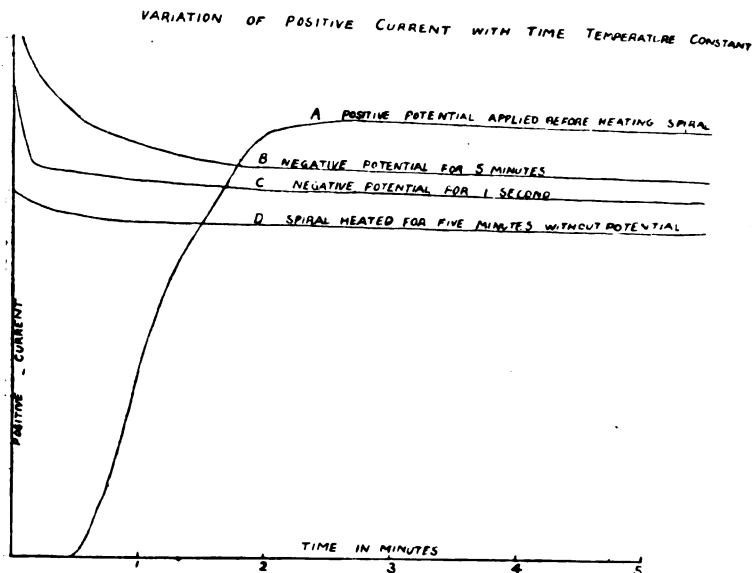
Fig. 6.



A considerable time would therefore elapse before the spiral had lost sufficient electrons to make the wire strongly electro-positive. When this condition was attained positive emission would be easier.

It is possible that even at the high temperatures at which the emissions take place there would be no positive emission unless the heated filament were discharging negative electrons. This point will be tested in experiments that are to be carried out with filaments surrounded by cylindrical electrodes.

Fig. 7.



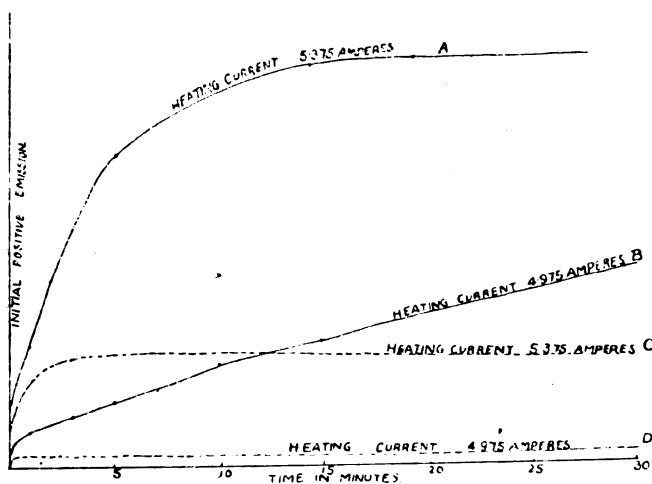
That the emission of electrons in large quantities prior to the positive emission measurements facilitates the discharge of positive electricity is shown clearly in figs. 7 and 8.

Fig. 7 shows the different types of curves that are obtained when the condition of the heated spiral prior to the measurements varies. Curve A is the normal type of curve obtained when the positive potential is applied to the spiral before the heating current is turned on. As described previously, the emission does not begin until after 30 seconds have elapsed, and the maximum is not reached until about three minutes have passed. Curve B shows the type of curve that is obtained when, instead of applying the positive potential before the spiral is heated, the spiral is first heated

and a negative potential assists the discharge of negative electrons for a period of five minutes and then the positive emission measurements are made. Here, instead of the initial positive emission current being zero, it is too great to measure with the galvanometer used, and remains above its normal value for a period of almost two minutes. Curve C is similar, the negative potential here being applied for a period of one second before taking the positive readings. Curve D shows the results obtained when the spiral is heated

Fig. 8.

VARIAION OF INITIAL EMISSION WITH TIME ELECTRON CURRENT
HAS BEEN FLOWING PREVIOUS TO MEASUREMENT OF POSITIVE EMISSION



for five minutes, but no potential is applied prior to the taking of the measurements of the positive emission. It will be noticed that here also there is a larger than normal value at first. The fact that the normal value of the emission gets gradually less in the four curves is due to the fact that the heating current in the spiral was gradually diminishing and its temperature therefore decreasing.

Fig. 8 illustrates more clearly the actual magnitudes of the initial emissions under the different conditions. In this graph the initial emission is plotted against the time that the spiral had been heated before the initial emission was measured. Curves A and B are for two different temperatures when, during the preliminary heating, the emission of

electrons was assisted by a negative potential of 220 volts. The dotted curves C and D are for similar temperatures when no potential at all was applied during this preliminary heating. It will be observed that in curves C and D a saturation value of the initial kick is soon reached, and that prolonged heating does not give rise to any further increase in the initial emission. This does not appear to be the case in curves A and B, and not only are the corresponding deflexions much larger than in C and D, but there appears to be no limit to the value of the initial kick, at any rate within the limits of the readings taken. For example, when the heating current was 4.975 amperes and the normal value of the positive emission a deflexion of 16 divisions, an initial deflexion of over 900 was obtained when a negative potential had been previously applied for a period of $2\frac{1}{2}$ hours. Moreover, not only was there a large discharge of positive electricity immediately after the long period of emission of negative electrons, but the deflexion did not fall down to its normal value for over an hour. It should be stated that the final steady value of the emission was independent of the initial condition. The fact that a saturation value is reached in curves C and D is probably explained by the fact that when no potential is applied the spiral will at first discharge negative electrons, but after a time the discharge will cease, owing to the spirals having attained a certain positive potential which will prevent further emission. There will be no such cessation of electron discharge when a negative potential is applied to the spiral.

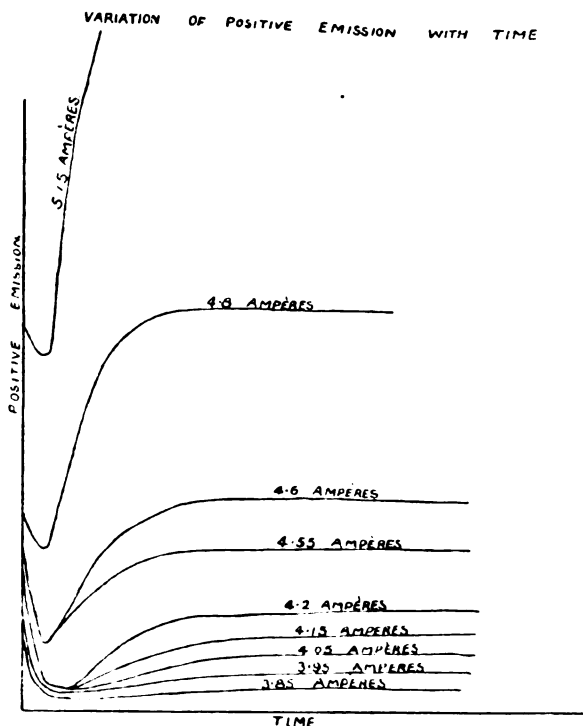
Fig. 9 shows the variation of the emission with time at different temperatures when the spiral had been heated for a few seconds only prior to the application of the positive potential.

It will be seen that in all the curves the emission drops to a minimum value after about 15 seconds and then rises to its normal value. The previous curves do not show this phenomenon, owing to the fact that the galvanometer in use was not sensitive enough to reveal it. When the more sensitive galvanometer was employed it was always observed.

It was thought at first that the initial emission might be due to the return of the space-charge to the heated spiral, but experiments upon this point negatived the idea. If, under the conditions of the experiment, the accumulated space-charge were sufficient to give a large kick to the galvanometer upon the application of a positive potential, then, if the heating circuit of the spiral were broken and the positive potential immediately applied, a similar kick should

be observed. Experiments on these lines, however, showed that the kick due to space-charge was not observable. One must assume, therefore, that the continued negative emission causes the accumulation of large positive charges upon the spiral, which are immediately expelled upon the application of a suitable potential. An alternative explanation is that the continued heating and emission of negative

Fig. 9.



electrons causes the expulsion of occluded gases ; but this does not seem to explain the phenomenon as well as the former hypothesis.

It is interesting to note that continuous positive emission over a period of 18 hours does not result in either prolonged increased negative emission or a large initial negative emission.

The following table of successive readings of the two
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currents illustrates the different behaviour with regard to this phenomenon:—

	Initial Emission.	Steady Value.
1. Negative Emission	0	100
2. Positive Emission taken after the negative current had flowed for 20 seconds	37	6
3. Negative Emission taken after the positive current had flowed for 6 hours	0	98
4. Positive Emission taken after the electron current had flowed for 2½ hours.....	256	6
	After 1 min. 40	

In the last reading the steady value was reached after a period of 13 minutes. In interpreting these tables it must be remembered that the electron emission is of a different order entirely from the positive emission, and that while the behaviour with regard to percentage changes is undoubtedly different in the two cases, an effect of the actual magnitude of the positive effect would hardly be observable when measuring the electron current. The reason why after large initial emission the discharge falls well below its normal value is not clear, and it is proposed to carry out further experiments upon this point.

Another matter of great importance is the value of the emission after what has so far been called the steady state has been reached. From the experiments carried out it has not been possible to ascertain whether prolonged emission results in a decrease in magnitude of the emission. The evidence tends to show that there is such a decrease with time, but exactly what is the rate of this decrease has not as yet been determined. With a Coolidge tube the currents required for heating the spiral to a high temperature are considerable, and in the case of the highest temperatures are well over 5 amperes. A slight diminution of current results in an appreciable decrease of temperature, and this is associated with a considerable diminution of positive emission. For accurate results it is necessary, therefore, to keep the heating current constant over long periods of time. Cells giving out a current of 5 amperes over a period of from 6 to 24 hours run down appreciably, and it is not easy to arrange for resistance to be cut out at such a rate as to keep the current absolutely constant. Periodic alterations of resistance are not satisfactory, as sudden alterations of temperature of the spiral, even though these changes be minute, cause anomalous and erratic results. Filaments which require a much smaller heating current will be better adapted

for experiments upon this point. The following tables show the type of results that have so far been obtained :—

TABLE V.

Approx. Current.	Applied Voltage.	Time.	Deflexion.
4.65	10.38	0	69
4.65	10.38	1 hr. 40 min.	63
4.65	10.38	2 hr. 30 min.	60
4.6	34	0	62
4.6	34	6 min.	61.75
4.6	34	10 "	63.5
4.6	34	15 "	63.5
4.6	34	23 "	64
4.6	34	30 "	61.5

In all experiments carried out the emissions followed the same curve. When the positive potential was applied before the spiral was heated, the emission gradually rose from zero to a maximum value, and thereafter apparently decreased very slowly with the time.

This maximum value is the value that has hitherto been called the steady value, as, in the case of all except the highest temperatures, it is by no means certain that the subsequent decrease is any greater than can be accounted for by the decrease in value of the heating current. In the above table the time zero is the time when this maximum value was reached.

If, however, the temperature be near the melting-point of tungsten, the positive emissions are very large, and there is undoubtedly a rapid decrease of the emission with the time, as is shown in Table VI. The values of the emission have

TABLE VI.

Approx. Current Heating.	Applied Voltage.	Time.	Deflexion.
5.85 amperes.	200	0	9300
5.85 "	200	3 min.	6300
5.85 "	200	6 "	5250
5.85 "	200	10 "	4350
5.85 "	200	15 "	3525
5.85 "	200	20 "	2910
5.85 "	200	30 "	2115
5.85 "	200	40 "	1605
5.85 "	200	60 "	1065
5.85 "	200	75 "	810
5.85 "	200	90 "	630
5.85 "	200	175 "	150

been adjusted so as to be on the same scale as in the preceding table.

With reference to the above table, it should be stated that, when after nearly three hours' heating the positive emission had decreased to the value shown, it was observed on reversing the potential that the electron current was very small, and immediately afterwards the spiral burnt out. Experiments upon prolonged emissions of both electrons and positive charges at temperatures near the melting-point would probably prove fruitful, but with Coolidge tubes would be rather an expensive proposition.

The Nature of the Positive Emission.

There seems to be little doubt that the current observed when a positive potential is applied to the spiral is due to the emission from the tungsten of particles carrying a positive charge.

It was suggested to me at first that the current might be due to photoelectric effect, the electrons being liberated from the tungsten anticathode by the incidence of the intense light emitted from the heated cathode. Such a photoelectric effect would, of course, increase rapidly with the temperature of the spiral.

The effect of the magnetic field upon the magnitude of the current and the experiments upon the growth of the current with time when the potential is applied before the spiral is lit up, rule out this explanation of the phenomenon. If it were a photoelectric effect, then the application of a magnetic field would probably destroy the current altogether, and, even if it did not destroy it, would certainly considerably diminish it. The general effect of the magnetic field is to cause an increase of the current at small potentials and a slight decrease at larger potentials and higher temperatures. This slight decrease at the higher temperatures may be owing to the fact that at these temperatures a small portion of the current is due to photoelectric action. Again, if the effect were photoelectric in origin, the rate of increase of the current with time would follow the curve of increase of temperature of the spiral. As soon as the maximum temperature was attained, the current would also reach a maximum, and would remain constant as long as the temperature of the spiral remained constant. The experiments with the electron currents show that the final temperature is reached after an interval not much greater than 15 seconds, whereas in some cases the maximum value of the positive current is not

attained until 6 minutes have elapsed. Further, the large initial emissions obtained after the spiral has been heated for some time or after the electron current has been flowing, would be difficult of explanation on the photoelectric hypothesis unless one assumes the presence of occluded gases within the spiral.

The obvious explanation of positively-charged particles emitted from the heated tungsten seems to be capable of accounting for all the phenomena observed. Even at the highest temperatures the number of these positive charges is only a small fraction of the number of negative electrons emitted, and until these electrons are prevented from passing between the electrodes, the current carried by the positively-charged particles cannot be observed. A high positive potential or a combination of a low positive potential and a magnetic field serves to eliminate the electron current, and leaves the positively-charged carriers open to observation.

If this explanation is the correct one, it is important that the nature and the origin of these positively-charged particles should be ascertained. With the apparatus available it was not possible to measure the deviation of these particles under the influence of a magnetic field, beyond observing that a field of 400 was not sufficient to prevent their passing between the electrodes. This points to the fact that the particles are either very heavy- or very slow-moving, or possibly a combination of the two. Previous work * on the production of ions from hot bodies indicates their existence (a) when there is residual gas in the apparatus or occluded gas in the metal, (b) when the metal is freshly heated in vacuo. These ions, however, are not positively-charged ions of the heated metal, although Thomson † has obtained evidence of the existence of positively-charged atoms of platinum emitted from heated platinum.

The present experiments reveal phenomena of an entirely different character from any previously observed. There is practically no residual gas in the tube, nor, so far as one can tell, is there occluded gas within the tungsten. The emission does not commence until a temperature of approximately 2500° C. is reached, and, so far as the writer is aware, this is considerably higher than in the case of previous experiments upon positive emission. Tungsten is, of course, the only common metal that can be heated to such a temperature, but it is possible that careful experiments upon metals at

* Richardson, 'Emission of Electricity from Hot Bodies,' pp. 196-250.

† Thomson, 'Conduction of Electricity through Gases,' 2nd ed., p. 220.

temperatures not far removed from their melting-point might reveal phenomena of a similar character. The positive emissions in the present experiments are affected by, and seem to be bound up with, the emission of large quantities of negative electrons. Unless one assumes that the electrons emitted are surplus atmosphere electrons moving about in the interatomic spaces, one must conclude that the emission of large numbers of negative electrons will leave behind positively-charged atoms of tungsten. At high temperatures there will be a tendency for these positively-charged atoms to evaporate and leave the metal. A suitable potential will assist this evaporation. It is known that at temperatures not far removed from the melting-point tungsten is surrounded by an atmosphere of tungsten vapour, for the spectrum shows reversed lines. The dragging away of these vapour atoms or molecules if they happened to be positively charged would, of course, be easy. The phenomena are not, however, due to normal evaporation alone, as the peculiar behaviour under prolonged observation indicates. The large initial emissions also point to a more complicated origin. After prolonged heating with a high negative potential applied, one might expect a large supply of positively-charged atoms both on the surface and within the metal.

The application of a positive potential would remove all the surface positively-charged atoms immediately, and for a considerable period there would be an abnormally large current, the length of the period being dependent upon the length of time the heated metal had been emitting large quantities of negative electrons. Afterwards a normal value should be reached. In the apparatus used the application of a high positive potential, although preventing the passing of electrons between the electrodes, would not prevent entirely the emission of electrons from the heated tungsten. In an apparatus where the heated filament was totally surrounded by the electrode and the application of a positive potential would prevent altogether the emission of electrons, it is possible that the positive emission would be either stopped or greatly diminished.

All the phenomena seem to be explicable upon the hypothesis that positively-charged atoms or molecules of tungsten are emitted from the heated spiral. The fact that a magnetic field of 400 gauss diminishes the emission slightly at the highest temperatures probably indicates that a small percentage of the particles are moving very slowly. A photoelectric effect at these high temperatures seems

improbable if the heated tungsten is surrounded by an atmosphere of vapour, for this atmosphere N would absorb any very short wave-lengths and prevent any light, that would be likely to give the observed effect, from reaching the anticathode. One must assume, then, the presence of very slow-moving positively-charged particles as well as faster-moving ones. The only alternative is to assume the existence of positively-charged electrons ; and as there is no evidence as yet of the existence of these, this hypothesis is not a desirable one.

Summary.

(1) It has been observed that at temperatures approaching its melting-point, tungsten emits positively-charged particles.

(2) These particles are probably atoms or molecules of tungsten.

(3) A magnetic field of 400 gauss only affects a small percentage of them.

(4) The magnitude of the emission of these positive charges increases rapidly with the temperature.

(5) If the heated tungsten previous to observation for positive emission emits large quantities of negative electrons, there is a large initial emission of positively-charged particles when the potential is reversed.

(6) The positive emission is of a different order from the electron emission, being much smaller.

(7) At the highest temperatures the positive emission decreases rapidly with time, but at moderate temperatures the decrease with time, if existent at all, is small.

(8) Certain tubes showed a diminution of the electron current near the point where the positive emission began. Others did not.

In conclusion I wish to express my thanks to Mr. Phanindra Nath Mitra for valuable help given in the carrying out of the experiments.

CIII. *The Entrainment of Air by a Jet of Gas issuing from a Small Orifice in a Thin Plate.* By J. S. G. THOMAS, D.Sc. (Lond. and Wales), A.R.C.Sc., A.I.C., Senior Physicist, South Metropolitan Gas Company*.

IN previous communications† particulars have been given of an experimental investigation of the discharge of air and other gases at various temperatures through a small orifice in a thin plate, and the entrainment of air by the jet of issuing gas. In particular it was shown that in the case of a lighter gas issuing into a heavier gas, the degree of air entrainment effected per unit volume of gas issuing in the jet was dependent both upon the density of the issuing gas and that of the air into which the gas issued. The experimental results were satisfactorily explained both qualitatively and quantitatively by assuming that the entrainment was effected in part as the result of a process of the nature of diffusion of the lighter issuing gas into the surrounding atmosphere. Thus it was shown that the volume V of air entrained (reduced to N.T.P.) per unit volume of gas issuing in the jet (measured under the experimental conditions of temperature and pressure) was given by

$$V = \alpha [\rho_1 + \beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{1/2}],$$

where α is the volume of air entrained by a jet of air of standard density, taken as the unit, issuing at the same excess pressure as the gas into air of equal density, β is the diffusion constant, and ρ_1 and ρ_2 denote respectively the density of the issuing gas and that of the gas into which the jet issues. The present communication deals with the dependence of the ratio V/α and hence of β upon certain of the experimental conditions, more especially upon the degree of restriction, by orifices or otherwise, of the amount of air entrained by the jet issuing under any specified excess pressure, and upon the diameter of the orifice through which the jet issues.

EXPERIMENTAL.

The apparatus corresponded very closely with that described in the latter of the two previous communications‡. The only essential differences were that the discharge tube (A) and the tube (D) into which the discharge issued were of

* Communicated by the Author.

† Phil. Mag. xlv. p. 969 (1922); xlv. p. 785 (1923).

‡ Phil. Mag. xlv. p. 785 (1923). The letters in the text refer to the figure given on p. 786 (*loc. cit.*).

somewhat smaller diameter than those specified therein, whilst the tube (E) through which air was induced by the jet was somewhat shorter.

The manner—if any—of the dependence of the value of the ratio V/α upon the degree of restriction of the air induced by the jet of gas was investigated by determining the amounts of air respectively induced by jets of air and hydrogen issuing from a specified orifice. The total amount of air induced was satisfactorily and easily varied by inserting brass diaphragms having different sized orifices in the induction tube (D). A few experiments were in like manner carried out with coal gas discharged through the jet orifice. These served to confirm results obtained with air and hydrogen. For the purpose of investigating the dependence, if any, of the value of the ratio V/α upon the diameter of the jet orifice, experiments were likewise carried out with a number of the jet orifices described in a previous paper*. The methods of experiment and deduction of results have already been sufficiently described. The temperature of the discharge was maintained constant at 13° C. to within $\pm 0.5^\circ$.

RESULTS AND DISCUSSION.

(1) *Character of the Aeration Curves relating Entrainment of Air to Pressure at the Jet Orifice.*

Curves representative of the results obtained when orifices of various diameters were inserted in the induction tube so as to restrict to a greater or less degree the amount of air induced by a jet of air or of hydrogen are shown in fig. 1, in which some of the experimental points have been omitted for clearness. Particulars referring to the diameter of the orifices so inserted and other details are given in Table I. The respective values of V/α were calculated from the experimental results as previously explained†.

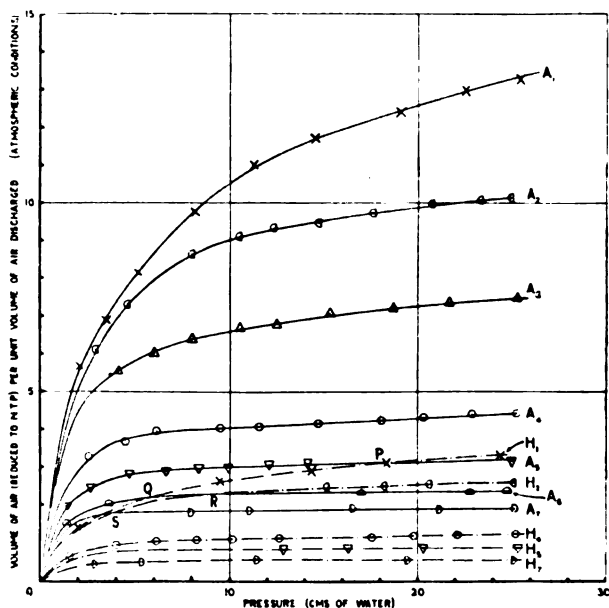
Referring to the curves A_1 to A_7 in fig. 1 relating to air entrainment by a jet of air issuing at various pressures, it is seen that as the degree of possible entrainment is restricted by the insertion of a smaller orifice in the induction tube, the aeration of the jet increases less rapidly with pressure, until in the case of curve A_7 the aeration of the jet is constant throughout the range of pressures 4 cm. to 25 cm. of water. This result is in marked contrast to the result indicated by curve A, representing results obtained with the

* Phil. Mag. xlv. p. 969 (1922).

† Phil. Mag. xlvi. pp. 792, 793.

open induction tube, which is typical of results contained in the two previous papers of this series. The manner in which the respective curves in their main portions increasingly approach to parallelism with the axis of pressures as the size of the orifice in the induction tube is reduced, is clearly seen from the respective values of the ratio of the aerations effected by the jet at pressures equal to 25 cm. and 2 cm. of water. For the series A_1 to A_7 , these values are respectively 2.42, 1.98, 1.67, 1.47, 1.43, 1.36, and 1.23. A corresponding result holds in the case of the curves H_1 to H_7 ; referring to

Fig. 1.



air entrainment by a jet of hydrogen. It would appear therefore that a constant or approximately constant value of the aeration at different pressures characterizes a flow system in which induction of air is effected under conditions such that the flow of the stream of air induced by the jet is considerably reduced from its normal value in free air either by restricting the effective area of the induction tube or otherwise. The results contained in Technologic Paper No. 193 (1921) of the Bureau of Standards relating to the design of atmospheric gas burners are of this character, and it would appear from what has been said, and from a consideration of the experimental method employed for

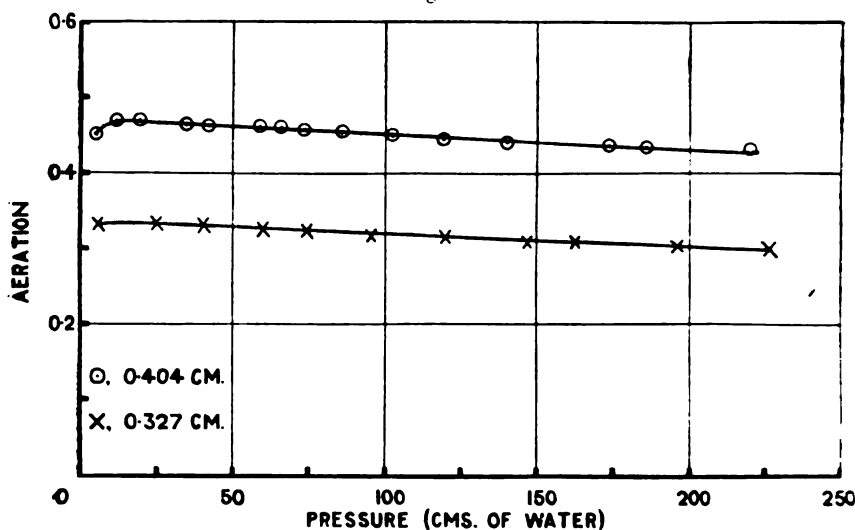
TABLE I.
Diameter of Orifice through which Jet of Gas issues 0.0607 cm.

No. of disk inserted in induction tube.	Diameter of orifice in disk in induction tube (cm.).	Total volume of air induced by air discharged at excess pressure 25 cm. of water (A) (c. ft. per hour).	Total volume of air induced by hydrogen discharged at excess pressure 25 cm. of water (H) (c. ft. per hour).	Ratio $\frac{H}{A}$	Mean ratio $\frac{V}{a}$ (from curves).	β .
1 (open tube)	2.025	24.1	20.9	0.87	0.233	0.713
8	1.911	23.9	20.9	0.88		
9	1.812	23.8	20.8	0.87		
10	1.714	23.0	20.2	0.86		
11	1.572	22.1	19.4	0.88		
12	1.496	21.0	18.4	0.88		
13	1.379	19.2	17.5	0.91		
2	1.271	17.6	16.5	0.94	0.257	0.724
3	1.023	12.9	12.7	0.98	0.265	0.740
4	0.763	7.6	7.68	1.01	0.270	0.739
5	0.634	5.48	5.54	1.01	0.274	0.770
6	0.544	4.04	4.20	1.04	0.276	0.737
7	0.482	3.19	3.37	1.06	0.285	0.824

measuring the air induced, that the results contained in that Paper are not applicable to conditions such as hold in the case of the operation of by far the greater proportion of atmospheric gas-burners, in which aeration is effected by the jet under what may be briefly referred to as "free induction" conditions, the minimum restraint consistent with the prevention of back-firing being imposed upon the induced stream of air.

It is of interest to examine the character of the aeration curves at higher values of the pressures at the jet. For this purpose experiments were carried out with coal gas discharged at pressures up to about 230 cm. of water through a circular orifice 0.1019 cm. diameter in a disk of thickness

Fig. 2.



0.265 cm. The induction tube was restricted by the insertion of an orifice of diameter either 0.327 cm. or 0.404 cm. The gas discharged through the orifice was measured by means of a high-pressure gas-meter made by Sugg, and was dried by passage over calcium chloride. The results obtained are briefly indicated in fig. 2. The ordinates represent the respective volumes of air (measured at N.T.P.) entrained per unit volume of coal gas in the jet, measured at atmospheric temperature and pressure. It will be noticed that at the comparatively high pressures employed in these experiments the degree of aeration of the jet decreased slightly and linearly as the pressure at the jet orifice was increased. The aeration of high-pressure jets will be discussed in more detail in a later paper.

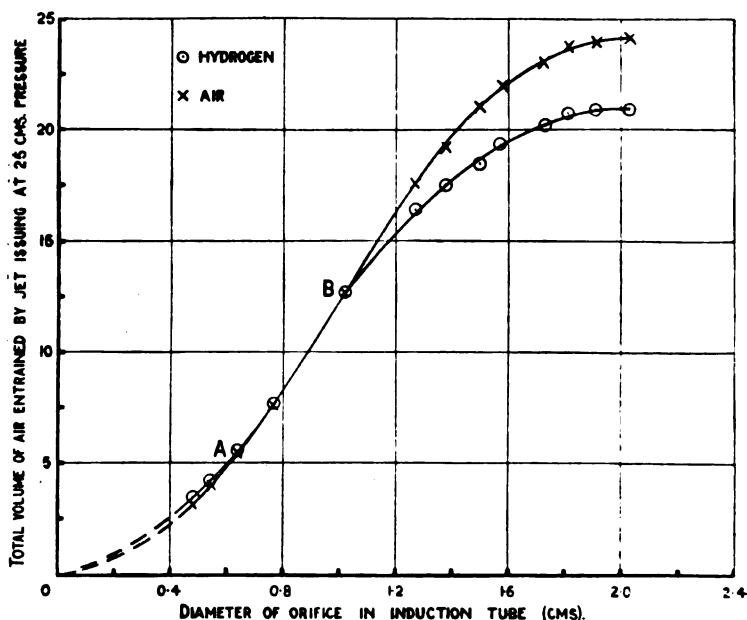
One other characteristic of the curves in fig. 1 may be referred to here, as it illustrates the difficulty experienced in the practical application of the results of aeration experiments carried out under specified conditions. Referring to curves H_1 and A_2 in fig. 1, the former relating to entrainment of air by a jet of hydrogen, no restriction being inserted in the induction tube, whilst the latter refers to entrainment of a jet of air issuing through the same orifice, the induction tube being restricted, it will be noticed that whereas for pressures at the jet less than about 19 cm. of water (see point P, fig. 1) the jet of air effects the greater degree of air entrainment per unit volume of the jet, for pressures above this amount the jet of hydrogen effects the greater degree of aeration. Similar crossing of curves relating to jets of hydrogen and air are seen at Q, R, and S. It is therefore clear that conclusions relating to aeration of jets of different gases operating at various pressures under different conditions as regards size of the induction tube cannot be drawn from results based upon observations made at a single value of the pressure.

(2) *Dependence of V/α upon the Degree of Restriction of the Amount of Air induced by the Jet.*

In fig. 3, experimental results given in columns 2 and 3. of Table I. have been plotted respectively as abscissæ and ordinates. The curve so drawn represents the dependence of the total volume of air entrained by a jet of air issuing under an excess pressure equal to 25 cm. of water through an orifice of diameter 0.0607 cm., upon the diameter of the orifice restricting air flow in the induction tube. A similar curve is drawn for a jet of hydrogen from the data contained in columns 2 and 4 of Table I. It will be seen that for values of the total volume of air entrained by the respective jets ranging from about 6.5 to 10 cubic feet per hour (see points A and B, fig. 3) the volumes entrained are practically equal in the case of the two gases. For greater values of the total entrainment, however, the air jet is the more effective, whilst for smaller values the hydrogen jet is more efficient. The maximum difference in the total entrainments effected by the respective gases under the conditions of the experiments amounts to only 13 per cent., which is small compared with the ratio of the respective densities of the two gases. We have in a previous paper ascribed the air-entraining power of a light gas issuing into a denser gas in part to diffusion of the issuing light gas into the denser surrounding atmosphere. The present result suggests that this process of diffusion of hydrogen occurs to

an increasing degree either as the *total* volume of air entrained by the jet under a specified pressure is reduced, or alternatively as the volume of air entrained *per unit volume* of the jet discharged under a specified pressure is diminished.

Fig. 3.



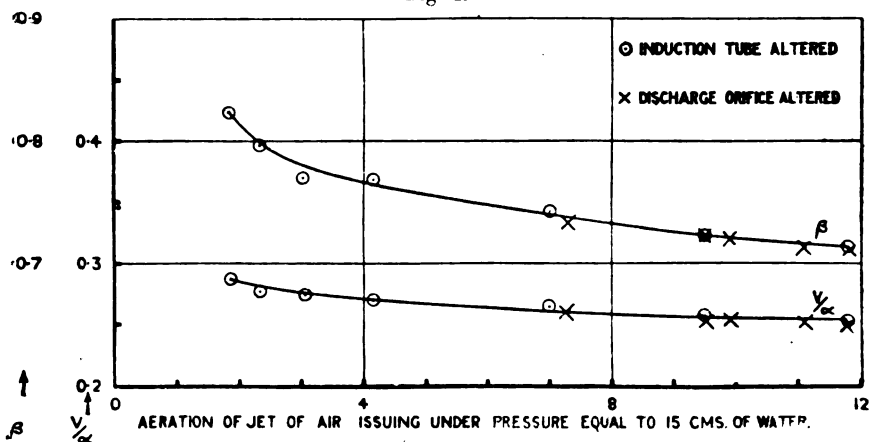
In fig. 4 the values of V/α contained in the sixth column of Table 1. have been plotted as ordinates against the respective volumes of air entrained *per unit* volume of air issuing from an orifice of diameter 0.0607 cm. under a pressure of 15 cm. of water. (This pressure was chosen in order that the results might be compared with later results in which the size of the orifice was altered.) The abscissae in fig. 4 therefore serve to indicate the relative restriction of the effective diameter of the induction tube produced by the insertion of the various disks referred to in column 2 of Table 1: Values of β have been calculated from the respective values of V/α by means of the equation

$$V/\alpha = \rho_1 + \beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{1/2},$$

account being taken of the temperature and pressure of the issuing gas and of the surrounding atmosphere at the time of the experiment. The values of V/α and β so determined are indicated by the symbol $\odot$ in fig. 4. The experimental values under which these values were

obtained were such that a *decrease* of the *total volume* of air entrained by the jet issuing under a specified pressure accompanied a decrease of the air entrained *per unit volume* of the jet. Results in which a *decrease* of the *total volume* of air entrained by the jet issuing under a specified pressure was accompanied by an *increase* in the volume of air entrained *per unit volume* of the jet are indicated by the symbol $\times$ in fig. 4. These latter results were obtained by the use of jets issuing through orifices of different sizes. We have previously shown* that a diminution in the size of the orifice through which a jet issues effects, under a specified excess pressure, a smaller total air entrainment but a greater air entrainment per unit volume of the jet. We see in fig. 4

Fig. 4.



that all the experimental points lie fairly well on a smooth curve, indicating an increase in the value of V/α and in the value of β as the aeration *per unit volume* of the jet issuing under a specified pressure decreases. We conclude therefore that in all cases the process of diffusion of hydrogen into the surrounding denser atmosphere occurs to an increasing degree as the aeration of the jet per unit volume under a specified pressure diminishes, irrespective of whether the decreased aeration is accompanied by an increase or decrease of the total volume of air entrained by the jet under the specified pressure. An increase in the value of β , *i. e.* in the diffusion effect, might be anticipated when the effective surface per unit volume of the jet is increased by diminishing the diameter of the orifice through which the jet issues. The results afforded by the present series of

* Phil. Mag. xlv. p. 984 (1922).

experiments indicate that the curves through the respective series of points (represented by $\odot$ and $\times$) are coincident within the limit of experimental error so that the magnitude of any such possible effect is in any case small, compared with the increase attributable to a decrease of the aeration per unit volume of the jet under a specified pressure as explained above. It is interesting to note that extrapolation of the upper curve in fig. 4 indicates that when the aeration of the jet is reduced to zero, the value of β is approximately unity.

SUMMARY.

1. It is shown that a constant or approximately constant value of the aeration of a jet of gas issuing at different pressures from an orifice, as referred to in Technologic Paper No. 193 (1921) of the Bureau of Standards, characterises an induction flow system in which the induction of air is effected under conditions such that the flow of the stream of air induced by the jet is considerably reduced from its normal value in free air by restricting the effective area of the induction tube or otherwise.

2. In the case of a gas issuing under comparatively high pressures and inducing air through a restricted flow system, the degree of aeration of the jet decreases slightly as the pressure at the orifice is increased.

3. In all cases, whether a diminution of the volume of air entrained per unit volume of a jet issuing under a definite pressure is accompanied either by a decrease or an increase in the total volume of air entrained by the jet, the process of diffusion of the lighter issuing gas into the surrounding denser atmosphere occurs to a greater degree as the volume of air entrained per unit volume of the jet diminishes. The results obtained indicate the very approximate equality of such increased diffusion effect derived whether from a decrease in the effective surface per unit volume of the jet or by reducing the effective diameter of the inductive flow system.

The experimental work detailed herein was carried out in the Physical Laboratory of the South Metropolitan Gas Company, and the author desires to express to Dr. Charles Carpenter and the Directors his thanks for the ready provision of all facilities necessary for carrying out the work.

Physical Laboratory,
South Metropolitan Gas Company,
709 Old Kent Road, S.E. 15.
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CIV. *Convective Cooling of Wires in Streams of Viscous Liquids.* By A. H. DAVIS, M.Sc.*

[From the National Physical Laboratory.]

Summary.

STUDY has been made of the cooling of wires immersed in streams of various liquids. *Theoretical considerations* point to a formula of the type

$$H/k = F(vdc/k; k/cv),$$

where H = Heat loss per unit time per unit length of the wire per degree temperature elevation,
 k = Thermal conductivity of the fluid,
 c = Specific heat of the fluid per unit volume,
 ν = Kinematical viscosity of the fluid,
 v = Velocity of the fluid stream,
 d = Diameter of the wire.

Since (k/cv) is practically constant for gases, the present experiments with liquids were undertaken to reveal its importance.

The *apparatus* consisted of a motor-driven whirling arm which carried the test-wire and forced it continually through the liquid contained in an annular circular trough. Observation was made of the temperature of the wire and of the electric energy necessary to maintain a measured temperature difference between the wire and the general body of the liquid. Wires of three sizes were used, and various *liquids* whose physical constants were measured.

The *results* show that the above formula is fairly satisfactory,

* Communicated by the Director of the National Physical Laboratory.
Phil. Mag. S. 6. Vol. 47. No. 282. June 1924. 3 Y

except that a factor must be included to cover certain small residual effects dependent upon d (and possibly upon θ) and due to some cause, possibly free convection, not fully investigated. It was found that the function F could not be represented by the product of two independent terms in $vd\epsilon/k$ and $k/c\nu$ respectively, but that each influences to some extent the effect of the other. The following form was found to be satisfactory:—

$$H/k = R \cdot f(k/c\nu) \cdot F\{(vd\epsilon/k) \times (k/c\nu)^{\frac{1}{2}}\},$$

where R represents the residual factors referred to. Curves are given showing the forms of the two functions. If they are represented by power terms thus, $f(x)=x^{-m}$ and $F(x)=x^n$, m and n vary with circumstances but lie within the limits given by $0 < m < 0.2$ and $0.38 < n < 0.48$.

Concise tables present the experimental results. An estimate was made of the *velocity of the natural convection current* set up by the heated wire.

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INTRODUCTION.

THE subject of the cooling of the surface of a hot body in contact with a moving fluid has received considerable investigation during recent years. For various reasons, diverse experimental methods have been used. Measurements have been made on the one hand of the heat which passes from the walls of a hot tube to the fluid flowing within it, and on the other of the cooling of wires and cylinders when immersed transversely in a fluid stream. In neither case does published information appear sufficient for determining the effect of the nature of cooling liquids: indeed, for the wire method, while air-cooling has been extensively studied, few other data are available at all.

Until liquids have received adequate attention, the laws of convection cannot be fully revealed. For convection of heat is ultimately a molecular phenomenon, which presents complexities in the case of liquids which are almost entirely absent when the gaseous state is considered.

A study has therefore been made of the cooling of wires when immersed in streams of various liquids of known physical properties.

I. THEORETICAL FORMULÆ.

Osborne Reynolds*, from the similarity of molecular motions involved in conduction of heat and diffusion of momentum (skin friction) indicated a relation between surface cooling and skin friction. His theory has received much attention in connexion with the turbulent flow in pipes. As Reynolds himself pointed out, its simplest form

* Reynolds, Proc. Manchester Lit. & Phil. Soc. (1874). See also Stanton, Report Adv. Comm. Aeronautics, p. 45 (1912-13).

requires supplementing by an additional factor relating to the transfer of heat through the eddy-free layer near the surface of the tube. G. I. Taylor* has recently calculated this correction from an estimate of the thickness of the film. He made use of the Lorentz criterion for steady fluid motion between two parallel planes moving tangentially to each other. His correction depends upon the ratio of the rates of diffusion of heat and of momentum in the fluid †.

Boussinesq ‡ was the first to give a formal theory of convection, and his analysis combined hydrodynamical equations with the Fourier equation for heat-flow. With certain assumptions he obtained, for similar bodies similarly immersed in infinite inviscid streams, a general solution which may be written in the form :

$$hl/k\theta = F(vlc/k), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where h = heat loss per second per unit area of the hot body,
 l = linear dimensions of the body,
 θ = temperature difference between the surface of the hot body and the distant fluid,
 v = velocity of the fluid stream,
 k = conductivity of the fluid,
 c = capacity for heat of the fluid per unit volume.

For horizontal wires of diameter " d ," transverse to the fluid stream, and of a length sufficient to render the effects of the ends negligible, the above equation may be written

$$H/k = F(vdc/k), \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

where H = heat loss per unit time per unit length of the wire per degree temperature excess.

For the case of such thin wires, and for non-turbulent flow, Boussinesq showed the form of the function to be given by a square-root law §. King ||, following him, calculated the form

$$H/k = 1 + (2\pi)^{\frac{1}{2}}(vdc/k)^{\frac{1}{2}} = 1 + 2.51(vdc/k)^{\frac{1}{2}} \quad . \quad (2)$$

for velocities above a (small) critical value. He assumed constant flux of heat across the surface of the wire.

* Taylor, Report Adv. Comm. Aeronautics, ix. p. 423 (1916-17).

† That is, upon the variable $k'cv$ referred to later in this paper.

‡ Boussinesq, *Comptes Rendus*, cxxii. p. 1382 (1901); cxxxiii. p. 257 (1901).

§ Boussinesq, 'Théorie analytique de la Chaleur,' t. ii. (1903). See also Russell, *Phil. Mag.* xx. p. 591 (1910), where exhaustive references are given.

|| King, *Phil. Trans. A.* ccxiv. p. 373 (1914).

Rayleigh*, in illustration of the use of the Principle of Similitude, derived an extension of the general formula, to include viscous fluids. The result may be written †:

$$hl/k\theta = F(vl/c/k; k/cv) \quad \text{or} \quad H/k = F(vdc/k; k/cv). \quad (3)$$

Nusselt ‡ in 1909 had already applied the principle to the problem of heat transfer in tubes, and had obtained a result of the same form. By a further assumption, he reduced his result to Boussinesq's form (equation 1).

Equation 3 forms the basis of the present work, where the effect of the k/cv term has been studied. An earlier paper§ showed how the expression follows from Boussinesq's method of analysis when a viscosity term is introduced.

II. EXPERIMENTAL.

1. INTRODUCTION.

Many experiments have been carried out on the heat-transmission to fluids flowing through hot pipes. Comparison with theory is not straightforward, since a certain length of leading-in pipe must be traversed before velocity conditions attain their final distribution ||. Leprince-Ringuet¶ made a study of experiments by many observers (Nusselt, Jordan, Stanton, Carcanagues, Ser, Pennsylvania Rrd, and Henry) and obtained a formula covering all results for air. However, no formula of Nusselt's simple type would include known values for other fluids, such as certain common gases, steam, and water. Stanton** found Reynold's formula to be satisfactory in certain respects, but to need correction presumably for the heat transfer through the eddy-free surface layer. The correction term evaluated by G. I. Taylor is a function

* Rayleigh, *Nature*, xcv. p. 66 (1915).

† This formula may equally well be written $hl/k\theta = F\{vl/v; k/cv\}$. In this form the relation to fluid-resistance formulæ is emphasized. The mechanical resistance R per unit area is given by $R_{or} = fvl/v$. Thus heat loss and mechanical resistance are closely related, provided allowance is made for complexity of fluid structure by means of a k/cv term.

‡ Nusselt, *Zeitschrift des Vereines deutsche Ingenieure*, Oct. 23, 1909.

§ Davis, *Phil. Mag.* xlv. p. 940 (1922).

¶ See Stanton, Report Adv. Comm. Aeronautics, viii. p. 16 (1916-17).

|| Leprince-Ringuet, *Comptes Rendus*, clii. p. 436 (1911).

** Stanton, Report Adv. Comm. Aero. p. 45, 1912-13. See also *Phil. Trans. A.* xc. p. 67 (1897).

of k/cv and appears promising*, but apparently more experimental data are required †.

McAdams and Frost ‡, in a survey of certain experiments on heat transfer in pipes, give a curve covering water and certain oils, in which the heat-loss ($hl/k\theta$) is a function of the hydrodynamical variable (rl/ν). Though the range of viscosity covered appears to be small (about 3-fold), this indicates that any other terms in the complete equation are of rather subsidiary importance.

Generally speaking, therefore, experiments with tubes appear to indicate that the complete formula for heat loss contains a k/cv term. The omission of this term yields simpler formulæ, which give results which are generally of the right order but which may differ quite appreciably from measured values.

As regards the heat losses from wires and cylinders in a stream of fluid, King § has made a very comprehensive study of the cooling of fine wires in air, covering a wide range of conditions. He found his results agreed excellently with a formula very similar to his own theoretical equation. A small correction term was necessary, depending upon the temperature excess θ of the wire; this he supposed to be due to variations in the physical properties of air as the temperature is changed. He found also that the dependence upon the diameter of the wire was rather *greater* than the theoretical formula suggested. His paper contains reference to similar work by other experimenters.

Hughes || experimented with large steam-heated cylinders up to 5 cm. diameter. His data do not fit King's special formula, as the variation with velocity ($v^{0.55}$ to $v^{0.7}$) is in excess of that given by a square-root law. However, the more general form of equation 1 appears satisfactory, except that variation with diameter in this case tends to be less than the formula requires. It is noteworthy that this deviation from the formula is in the opposite sense to that found by King for his wires.

The range of published data is further extended by the results of Kennelly and Sanborn ¶, who used air at various pressures. Some earlier results by Kennelly** cover some

* Taylor, *loc. cit.*

† Stanton, Report Adv. Comm. Aero. p. 16, 1916-17. See also Pannell, p. 22.

‡ McAdams & Frost, Journ. Ind. Eng. Chem. xiv. p. 1101 (1922).

§ King, *loc. cit.*

|| Hughes, Phil. Mag. xxxi. p. 118 (1916).

¶ Kennelly & Sanborn, Am. Phil. Soc. Proc. liii. p. 55 (1914).

** Kennelly, Trans. A.I.E.E. xxviii. (1) p. 363 (1909).

of the range later studied by King, but include additional data for a larger wire.

The present author* has given a graph upon which results of these experimenters have been plotted, and it appears that equation 1 *a* is fairly satisfactory, viz. :

$$H/k = F (vdc/k) \dots \dots \dots (4)$$

However, since k/cv is practically a constant for gases, such experiments cannot reveal the effect of this term. Practically no values are available for liquids, and the need of the present investigation is thus clear.

2. CHOICE OF METHOD.

The following general considerations led to the choice of the present method of investigating the cooling powers of streams of liquids. By using wires as the hot bodies size was easily altered, and by adopting electrical heating measurements of temperature and heat loss were readily made. By moving the wire through the liquid instead of the liquid past the wire, complications were avoided due to non-uniform flow in tubes and troughs, for in these the flow is greatest in the centre and is not steady until considerable lengths have been traversed. An annular circular track was used; it has various advantages. Since some general circulation of the liquid was of course set up, the velocity distribution question was not entirely eliminated, but was only of secondary importance, as it only affected a correction term which had to be applied to the observed speed of the wire.

3. APPARATUS.

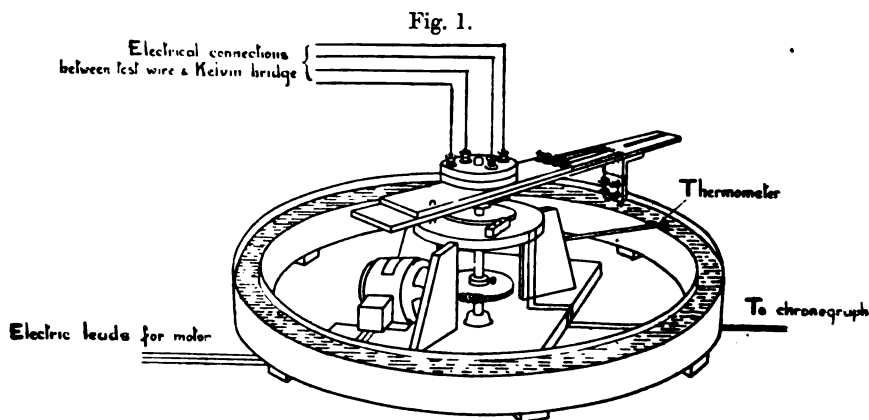
The apparatus used consisted of a motor-driven whirling arm which, by suitable attachments, carried the test wire in a vertical position and forced it continually through the liquid contained in the annular circular trough. Observation was made of the velocity of the wire and of the electric energy necessary to maintain a measured temperature difference between the wire and the general body of the liquid. The energy dissipation was determined from the observed current through the wire, and from its resistance as obtained by means of a Kelvin double bridge. This resistance gave also the temperature of the wire.

* Davis, Phil. Mag. xli. p. 899 (1921).

(i.) *The Whirling Arm and the Trough.*

The general arrangement of the apparatus is shown in fig. 1.

A balanced whirling arm was driven through a worm and wheel (ratio 100 : 1) by means of a 1/10 horse-power electric motor, fitted with ball bearings. The motor was shunt-wound, and the speed was controlled by means of a series resistance in the armature circuit. To avoid communication of vibration to the rotating arm, the motor was separately screwed down to the concrete floor. Considerable care was taken to ensure uniformity of motion, even at low speeds, throughout a complete revolution of



The Whirling Arm and the Trough.

the whirling arm. The motor was driven by means of a storage battery. The rotating arm was fitted with a friction brake to reduce to a minimum the effect of any frictional variations in the bearings. (A thrust-ball bearing took the weight of the rotating arm.) The shaft was accurately vertical, so that the rotating arm had no lowest position at which it would tend to stop during a revolution even if the balance were not exact. A spirit-level, used on the arm at various positions of a revolution, was useful in this connexion. All woodwork was painted or varnished to avoid defective alignment arising from warping.

The annular circular trough was made from sheet brass (0.16 cm. thick), and was supported separately from the concrete floor to avoid vibrations and ripples. Porcelain supports afforded thorough electrical insulation. The cross-section of the trough was 7 cm. wide and 11 cm. deep.

The test wire moved centrally in the trough, the circumference of the circular path being 242 cm. No serious difficulty was experienced on account of any variation in the width of the trough at different parts of the circumference. Some slight imperfection in this respect merely caused the galvanometer-spot to wander slightly from side to side during a revolution of the arm, instead of remaining exactly at zero all the time. Measurements of the general swirl of liquid in the centre of the trough were made at various points of the circumference, but no serious divergences from the mean were observed.

During the motion of the rotating arm the surface of the liquid was disturbed by the passage of the wire, but the effect was soon damped out and the surface was smooth again before the arm re-passed the same point on its next revolution. The wave behind the arm was especially pronounced for water, but even then, except at highest speeds (about 55 cm. per sec.), the disturbance did not persist for the time taken by the arm in a complete revolution.

Undoubtedly the use of an annular trough rather than a simple circular bath tended to reduce the amount of swirl set up as well as the persistence of these surface-disturbances.

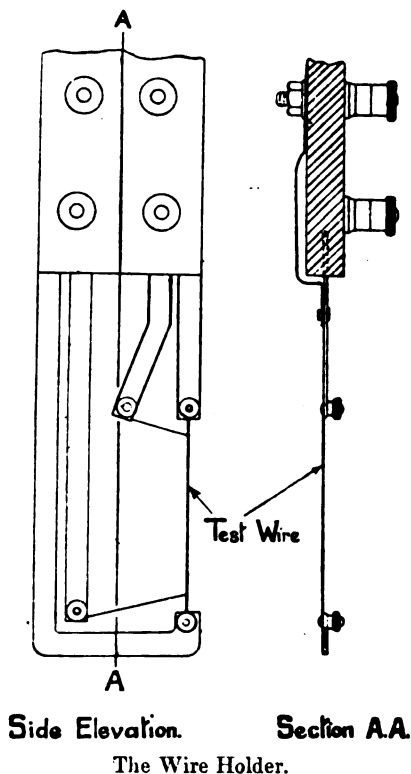
(ii.) *The Wire Holder.*

Details of the holder used for the test wire are shown in fig. 2. It was made from brass strip ($\frac{1}{4}$ in. $\times$ $\frac{1}{16}$ in.), together with suitable terminals and an ebonite support. The holder was sufficiently springy to keep the wire gently taut, when adjusted to proper length between the terminals. Provision was made for potential and current leads. The strip moved edge-first through the liquid, and the section thus presented was found to be sufficiently stream-line in shape to be satisfactory for the velocities used.

It will be seen from the figure that the two long supporting strips were placed an inch or so behind the test wire. It appears that at the side or in front they would have been more likely to interfere with the stream past the wire. Visual observation of the motion through liquids confirmed the opinion that, upstream, the effects of the strip were limited to only a few millimetres. The arrangement adopted had the additional advantage that the whole of the immersed parts were moving centrally in the trough,

so that the velocity distribution in the fluid was simpler, the trough could be made narrower, and economy was thus effected in the quantity of liquid used.

Fig. 2.



(iii.) *Electrical Measurements.*

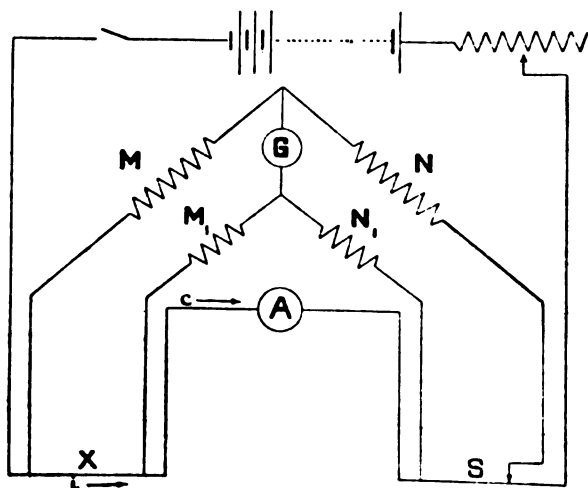
With regard to the electrical measurements, a dual arrangement was fitted up so that two methods could be used. In one a specially-constructed Kelvin bridge was used, and for the other a calibrated potentiometer was available with suitable standard resistances. On account of its greater convenience, the Kelvin-bridge method was almost invariably adopted for each series of observations; but the potentiometer was permanently installed so as to be readily available for checking the bridge, the resistances of its slide-wire and coils, and the accuracy of the ammeter.

However, for paraffin and for air, a series of potentiometer observations of heat-loss were made, and they agreed satisfactorily with those obtained by means of the Kelvin bridge.

(iv.) *The Resistance Bridge.*

Fig. 3 is a diagram of the connexions of the Kelvin bridge. The arm X represents the platinum wire under test, which was compared with the variable standard resistance S. This standard consisted of a number of 0.05-ohm

Fig. 3.



The Kelvin Bridge Connexions.

coils of heavy manganin wire (S.W.G. 11), together with a 0.1-ohm slide wire 160 cm. long. It had been carefully calibrated by a potentiometer method to read to one ten-thousandth part of an ohm. The ratio arms M, N, M₁, and N₁ contained accurately adjusted coils of 100 ohms each, together with leads which, although they were of small resistance ($\frac{1}{2}$ ohm), had also been adjusted to sufficient equality (1 per cent.) to avoid appreciable errors which otherwise might have been introduced.

To provide electrical connexions to the wire X on the rotating arm, slip rings were utilized, similar to those described by King*, consisting of stationary copper rings

* King, *loc. cit.*

dipping into rotating mercury troughs. The resistance introduced into each arm by the slip-ring apparatus was less than 0.003 ohm, and it remained constant to less than 0.0001 ohm whether the arm was rotating or still.

The ammeter A was a Weston Laboratory Standard instrument. The galvanometer G was a reflecting instrument of the moving-coil type, very free from troublesome zero-drift. Its sensitivity was such that 1 microampere gave a deflexion of 50 millimetres on a scale at a distance of 1 metre from the galvanometer. The full sensitivity was required only when the initial resistance of the cold wire was determined, and it was suitably reduced when the heating currents were used.

When the bridge was balanced the various resistances satisfied the following formula :

$$X = \frac{M}{N} S + \frac{AN_1}{A + M_1 + N_1} \left(\frac{M}{N} - \frac{M_1}{N_1} \right). \quad . \quad . \quad (5)$$

The current c measured by the ammeter was not exactly the same as that i through the test wire. Strictly a correction was necessary according to the equation

$$i = c \left(1 + \frac{A}{M_1 + N_1} \right); \quad . \quad . \quad . \quad (6)$$

but A was usually so small that the correction was negligible.

With the bridge out of balance by an amount dX in the test wire, the galvanometer current (g) was given approximately by the formula

$$g \left\{ 2 + G \left(\frac{1}{M} + \frac{1}{N} \right) \right\} = \frac{cdX}{M}. \quad . \quad . \quad . \quad (7)$$

(v.) *Precautions and adjustments.*

At the outset the apparatus was well insulated. It was tested by means of an Evershed "Megger" Insulation tester, and also by observing whether the galvanometer remained at its true zero when only one pole of the battery was connected to the apparatus.

Thermoelectric effects were practically negligible. The connexions of the platinum test wire were all immersed in the liquid in the trough, and were thus at constant temperature. The rest of the bridge connexions were of copper or manganin, and these metals together exhibit little thermoelectric activity. Some slight effects were found on one or two occasions, but they were only appreciable when getting the original balance with a small current: they were eliminated by the familiar

device of working with the galvanometer circuit always closed, and adjusting the bridge so that no deflexion occurred when the battery was reversed. Reversals with the large currents showed no change of balance conditions.

To keep the current as steady as possible the source of supply was a 110-volt storage battery in series with a ballast resistance.

The complete ratio arms M and N, consisting of coils and leads, were accurately adjusted to equality in the following manner. The coils themselves were tested for equality by reversal of connexions, and found to be satisfactory. The potential leads from the coils, which are also in the ratio arms, were brought to equality by adjusting so that the balance of the bridge was not appreciably disturbed if the coils were short-circuited by plug contacts, thus leaving the leads themselves as the complete outer ratios of the bridge. The inner ratio arms were then similarly treated. This procedure ensured that the ratios M/N and M_1/N_1 were accurately equal to unity, and so resulted in the simple relation $\bar{X} = \bar{S}$, independent of the intermediate resistance A. It was experimentally verified that increasing A fivefold (from 0.2 ohm to 1.2 ohm) did not affect the reading by more than one part in 3000 (see equation 5). It was easy to make adjustment of this accuracy whenever the test wire was changed, and the apparatus was frequently checked in this and in other ways during use.

As an overall test of the bridge, a standard 0.1 ohm coil was substituted for the test wire. The Kelvin bridge indicated the correct resistance for this, and the reading was the same for large currents (5 amps.) and for very small ones (0.07 amp.); was independent of whether the arm was rotating or not; was not influenced by the speed; and was also independent of the direction of the current employed. This is a stringent test of the suitability of the bridge and slip rings for the currents involved, and of freedom from errors due to leakage or thermoelectricity.

It remained only to substitute the actual test wire and holder for the standard 0.1 ohm coil, and to test for the absence of thermal effects and leaks by observing the behaviour of the galvanometer spot on reversal of the various currents and upon switching off completely.

(vi.) *Procedure during an experiment.*

To obtain a series of observations the usual procedure was as follows. With the test wire in position, and with a small current through the wire (0.07 amp.), the bridge was

balanced by adjustment of the position of the slider along the slide wire. As the heating effect of such a small current was negligible*, this reading gave the resistance of the wire at the temperature of the oil.

The slider position was then altered to increase the reading by a definite amount dR . This disturbed the balance of the bridge. With the arm rotating at measured speed, note was made of the increased current through the wire necessary to restore the balance. From the constants of the test wire the increment of temperature associated with the resistance dR was known, and the heat loss from the wire at this speed was readily calculated.

This procedure was repeated with the same value of dR , but with several different speeds. Further series were then taken, until a range of values of temperature excess and velocity had been obtained.

During a series of experiments, the initial temperature of the liquid sometimes drifted slightly. This was allowed for by slight change in the initial slider position, so that dR was maintained constant throughout, and the drawing of a series of curves was facilitated.

It was important to remove stray suspended fluff from the liquid under test, for otherwise readings could not be taken owing to a pronounced drift of the galvanometer reading. It was astonishing how much fine fibrous material could gain entrance to the liquid, and equally remarkable that the galvanometer spot could indicate so readily when a single fibre, almost invisible, became attached to the moving wire. Consequently all liquids used were passed through filter-paper two or three times, and collected in large clean glass vessels. Before each filling, the experimental trough was very carefully cleaned with suitable agents and swilled out with petrol. A blowpipe-flame was then passed rapidly over the interior to burn off any adherent fibres, and the trough was again washed out, first with filtered petrol and finally with a small quantity of the liquid to be tested. Except when experiments were actually in progress the trough was kept covered, and at all times unnecessary disturbance of the air of the room was avoided.

Even with these precautions fluff was not completely eliminated, but the trouble was not serious. Consistent results were obtained by cleaning the test wire gently with another wire just before taking readings, after a preliminary run had shown the probable values. Half a minute or more

* It was satisfactory to find the balance independent of whether the wire was moving or not.

was required in taking a final reading, largely because the steady swirl of liquid could not be attained in less time. At times conditions were obtained which were practically steady (water for instance), but at others there was sufficient suspended material to give a slight drift. For instance, on one occasion with No. 1 oil and the 6 mil wire there was a drift equivalent to about a $\frac{1}{2}$ per cent. change in heat loss in one minute, and no further change in the next two minutes. Repeated experiments on this occasion indicated that results for all temperatures of the wire were certainly reproducible to within ± 2 per cent., and usually variations were of the order of ± 1 per cent. or less. If the difficulties increased appreciably, refiltering was resorted to and an improvement thus effected.

(vii.) *Measurement of Velocity.*

No difficulty was experienced in determining the velocity of the rotating arm. The periods for one revolution varied from 3 seconds to 25 seconds. An electrical buzzer recorded each revolution, and it was usually sufficient to time with a stop-watch a convenient number of revolutions. A chronograph arrangement connected to a standard clock was available, but was not necessary for general use. A stroboscopic arrangement could have been used for observing the constancy of the actual speed of the motor during a complete revolution of the arm, but was not required, the galvanometer spot being sufficient indication of the state of affairs.

To obtain the velocity of the wire relative to the liquid, it was necessary not only to measure the velocity of the rotating arm, but also to evaluate the correction for the general circulation of the fluid through which the wire moved.

To measure the swirl velocity the test wire was removed from the rotating arm and mounted vertically in a fixed position in the centre of the trough, so that a dummy wire attached to the rotating arm passed within a millimetre or so from it. Heat losses from the wire in this position were measured with the arm rotating at various speeds, and compared with the losses experienced when it was mounted upon the rotating arm itself. The method of deducing the swirl velocity from the results is as given below.

For a given temperature excess, whether the wire is mounted on the rotating arm or is fixed in the centre of the trough, the heat emitted from it depends only upon the motion of the wire relative to the stream of liquid.

If V_a is the velocity of the wire attached to the moving arm, and if V_s is the velocity of the swirl of liquid set up, the velocity V of the wire relative to the fluid is given by $V = V_a - V_s$.

If the swirl velocity is proportional to the arm velocity causing it, then the relative velocity also will be proportional to V_a and we may write $V_r = kV_a$.

If now we find (from graphs) the new arm velocity V_{a_1} , with which the moving wire must move to give the same heat loss as was experienced by the swirl wire, we have $V_s = kV_{a_1}$. Hence the correction factor k may be calculated, and we find $k = V_a / (V_a + V_{a_1})$.

Results obtained are given in Table I., together with check values obtained by another method. The wire data indicate that k is practically constant for a given liquid,

TABLE I.
Swirl velocity of Fluid expressed as percentage of the measured wire velocity.

Liquid.	Method.	Arm velocity (cm. per sec.).				Mean value taken.
		10	20	50	70	
		per cent.	per cent.	per cent.	per cent.	per cent.
Water	Wire	...	...	18	18*	} 18
	Speck	14	17	21	21*	
Paraffin	Wire	...	...	16	16	} 16
	Speck	20	20	19	17	
Oil No. 1 ...	Wire	...	...	15	17	} 17
	Speck	17	17	17	18	
Oil No. 2 ...	Wire	...	...	15	15	} 15
	Speck	10	14	19	19	
Oil No. 3 ...	Wire	...	...	12	12	} 12
	Speck	10	11	15	16	

* For these speeds the surface waves had not subsided before the wire came round again.

and that the mean relative velocity was between 82 per cent. and 88 per cent. of the measured arm velocity. The velocity distribution near the centre of the trough was also found to be fairly uniform, and it did not vary appreciably in different parts of the circumference. In the experiments, conditions were fairly steady except at the moment when the rotating arm passed the swirl wire; precautions were taken to break the galvanometer circuit momentarily as this took place, and

the swirl values obtained refer to the general circulation in the centre of the trough.

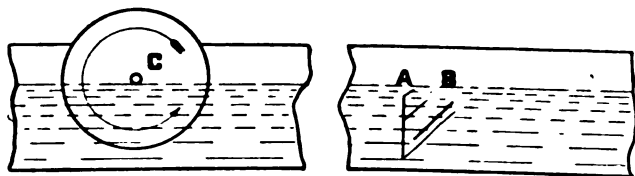
The method adopted as a check on the wire method was not so convenient, but it revealed visually the nature of the flow. The arm was set rotating in the usual way, and when the circulation of liquid in the trough was steady observation was made of the motion of a speck of floating or suspended dust. For some cases tobacco ash was found to be very convenient. The swirl velocity measured was the general drift. The timing of the speck was commenced sufficiently long after the passage of the test wire for the flow to be normal, and was completed just before the returning wire brought the local disturbances round again. Simultaneous observation of floating specks and suspended particles confirmed that there was a central core of liquid $\frac{1}{2}$ in. to $\frac{3}{4}$ in. wide, through which the test wire was moving, where the velocity was practically uniform and independent of depth.

The agreement between these check values and those obtained by the wire method was quite good, as may be seen from Table I., though generally the speck method gives higher results. It will be seen that generally the mean value taken is that given by the wire, although some attention has been paid to the other results. Divergences from the mean are not very systematic, and appear to have an effect on the true velocity of the order of ± 2 per cent.

(viii.) *Velocity of the Natural Convection Current from the Wire.*

Experiments were carried out to ascertain to what extent the natural convection current from the heated wire was comparable with the velocity of the wire relative to the liquid.

Fig. 4.



Arrangements for determining the Velocity of the Natural Convection streams from the hot wire A.

The principle of the method of measuring the velocity of the natural convection current is simple, and is illustrated in fig. 4. The heated wire was mounted vertically at a position A in the trough. A steady circulation of liquid

past the wire was maintained by means of the paddle-wheel C, placed as far away as possible. Convection currents from the wire could then be observed as apparently straight filaments adherent to the wire and trailing behind it at an angle to the vertical depending upon the velocity of the liquid in the trough. Observation was made of the stream velocity at which the filaments were inclined to the vertical at an angle of 45° . In this case, heated particles of liquid were moving so that the vertical component of velocity, due to natural convection, was equal to the horizontal component, which was known from the observed liquid speed.

Errors of refraction in the estimation of the angle of 45° were avoided as follows. A separate piece of wire B was suitably attached to the apparatus, so that it was immersed in the liquid and extended upwards behind the heated wire at this required angle. Speed adjustments were made until the fluid filaments were parallel to it.

These apparent filaments were of course due to the altered refractive index of the liquid which had been heated by the wire. No difficulty was experienced in seeing them with some of the coils. However, with water practically nothing could be detected; so in such cases a speck of soluble dye was attached to the wire at one point. It was quite easy to attach such a speck when desired, introducing it on the end of another piece of wire.

Only the order of the effect was desired, so elaborate arrangements were not adopted. However, by using a transparent trough with plane sides, photographs could be taken and greater precision attained. The results might be of some interest apart from their present application.

The velocities of the natural convection current were measured for water, No. 2 oil, and paraffin. They were more or less proportional to the temperature excess of the wire, and were respectively 0.01, 0.006, and 0.02 cm. per sec. per degree temperature excess of the wire.

The maximum temperature excess used in the main experiments was about 70°C ., whence natural convection streams of the order of $\frac{1}{2}$ to $1\frac{1}{2}$ cm. per sec. are to be expected. These should cause but little error in estimating the velocity of the fluid relative to the wire, for being vector quantities directed at right angles to the motion of the wire, they would only increase the slowest speed (10 cm. per sec.) by about 1 per cent. At higher speeds the effect should be quite negligible.

4. THE LIQUIDS USED.

(i.) *Their nature and condition.*

The cooling power of five liquids was studied. These were distilled water, paraffin, and three transformer oils, of which the most viscous resembled olive oil at 15° C. and became practically solid at 8° to 10° C. Thus a wide range of viscosity (and of k/ν) was covered, and the fluids had the advantage of being of kinds frequently used for cooling purposes. Transformer oils are very carefully refined products. Special care had been taken to ensure that they were dry, clean, and unmixed with other oils or samples, and in a condition satisfying the stringent requirements of their normal use.

Reference has already been made to the care taken to remove fibres of fluff and suspended particles. It was also observed that innumerable bubbles filled the oils when they were freshly poured into a vessel. These would have caused errors in some of the tests, so the liquids were poured carefully and time was allowed for the bubbles to disappear. This delay also allowed the temperature to settle down.

(ii.) *Physical Properties of Liquids used.*

The following outlines the various methods used in measuring for these liquids the physical properties concerned in convective cooling. The results obtained are given in Table II.

(a) * *Density (ρ).*

Determinations of density were made at temperatures of about 15° C., 50° C., and 80° C., an ordinary specific gravity bottle being used. Values for water were taken from tables.

The coefficients of expansion, of importance in natural convection, may be deduced from these results.

(b) * *Viscosity (η) and Kinematical Viscosity ($\nu = \eta/\rho$).*

Determinations of viscosity were made at various temperatures. Values for water were taken from published tables. For the more viscous oils a Redwood (No. 1 type) viscometer was used in accordance with customary practice at the National Physical Laboratory †. Essentially the method consists in determining the time taken for 50 c.cs. of the oil at the test temperature to flow out of an oil cup through a

* Mr. A. R. Challoner assisted with these observations.

† Higgins, 'N. P. L. Collected Researches,' xi. pp. 1-16.

suitable capillary jet, the initial level of the oil having been accurately adjusted to a certain standard position. In this way "kinematical viscosity" is determined, from which the other coefficient may be calculated.

TABLE II.
Physical constants of Liquids used.

Liquid.	Temp. ° C.	ρ .	$10^4 k$.	η .	ν .	$\frac{\eta}{k}$ $= c\nu/k$.	s .	c .
Water	12	1.00	14.0	0.0124	0.0124	8.86	1	1.00
	15	1.00	14.0	0.0114	0.0114	8.15		1.00
	20	0.998	14.0	0.0101	0.0101	7.2		1.00
	40	0.992	14.7	0.0066	0.0066	4.48		1.00
	50	0.988	15.0	0.0055	0.0056	3.67		0.99
	75	0.975	...	0.0038	0.0039	...		0.98
	80	0.972	...	0.0036	0.0037	...		0.97
Paraffin	12	0.814	3.0	0.0220	0.0270	38.1	0.52	0.42
	15	0.812	3.0	0.0208	0.0256	36.0		0.42
	20	0.809	3.0	0.0189	0.0234	32.6		0.42
	50	0.787	2.8	0.0110	0.0140	20.4		0.41
	60	0.780	2.7	0.0096	0.0121	18.5		0.41
	75	0.769	2.6	0.0078	0.0101	15.6		0.40
	80	0.765	...	0.0075	0.0096	...		0.40
Transformer Oil No. 1	15	0.844	3.2	0.140	0.166	205	0.47	0.40
	20	0.841	3.2	0.116	0.138	170		0.40
	50	0.821	3.1	0.046	0.066	70		0.39
	60	0.814	3.1	0.036	0.044	54		0.38
	75	0.804	3.1	0.027	0.033	40		0.38
	80	0.801	...	0.026	0.032	39		0.38
Transformer Oil No. 2	12	0.876	2.9	0.442	0.505	732	0.48	0.42
	15	0.875	2.9	0.384	0.438	633		0.42
	20	0.872	2.9	0.303	0.347	500		0.42
	50	0.852	2.9	0.090	0.106	149		0.41
	60	0.846	2.9	0.063	0.074	104		0.41
	75	0.836	2.85	0.041	0.049	69		0.40
	80	0.833	...	0.035	0.042	...		0.40
Transformer Oil No. 3	12	0.918	3.0	0.981	1.07	1500	0.46	0.42
	15	0.915	3.0	0.745	0.816	1142		0.42
	20	0.912	3.0	0.506	0.555	776		0.42
	50	0.894	2.9	0.121	0.135	191		0.41
	60	0.888	2.9	0.084	0.095	134		0.41
	75	0.879	2.9	0.059	0.067	93		0.40
	80	0.876	...	0.052	0.060	83		0.40

For paraffin, the Redwood instrument is not suitable, as the flow would be turbulent. In this case the viscosity was measured by comparison with water in an Ostwald viscometer*. This consists of a marked U-tube, the connecting

* I am indebted to Dr. G. Barr, of the Dept. of Metallurgy and Metallurgical Chemistry, for this determination.

piece being of capillary dimensions. The liquid under test stands initially at different levels in the two limbs, and the time is noted which elapses while the liquid meniscus passes certain marks on the tube.

It is desirable to notice (see Table II.) that very considerable viscosity changes arise when the temperature of a liquid is altered.

(c) *Specific Heat (s) and (c).*

The specific heat (s) determined for each oil was the mean value over the range 20°C. to 100°C. It was obtained by the method of mixtures, a measured quantity of the oil under test at a temperature of 100°C. being poured into a calorimeter containing a standard oil at 20°C. The specific heat of the oil chosen as standard had been determined at air temperatures by introducing a copper block at 360°C. into a measured quantity contained in a calorimeter. The standard oil was found to have a specific heat at air temperatures indistinguishable from its mean value over the range 20° to 100°C. Values obtained were reproducible to an accuracy of about 2 per cent.

The capacity for heat (c) per unit volume of a liquid is given by the equation $c = sp$.

(d) *Thermal Conductivity (k).*

Thermal conductivities of the fluids were determined by means of an apparatus similar to that described by Goldschmidt*. The method consists of stretching a fine platinum wire along the axis of a small horizontal silver tube full of the test liquid, and measuring the electric current necessary to maintain a measured temperature difference between the wire and the walls of the tube. This gives a relative value for the conductivity of the oil, for it appears that with fine wires, small tubes, and but slight heating the disturbing effects of convection currents are negligible. This is not surprising since the cooling of a fine wire immersed horizontally in a bath of fluid tends to depend only upon the conductivity of the fluid in these conditions.

In the actual apparatus the silver tube, 2 mm. diameter and 12.7 cm. long, was fitted tightly into a massive copper cylinder of 5 cm. diameter, so that the temperature was uniform throughout its length. A 4 mil platinum wire, with current and potential leads attached to its ends, was adjusted

* Goldschmidt, *Phys. Zeits.* xii. p. 417 (1911).

to pass axially through the tube. Since the current leads were helical copper springs they prevented sagging of the test wire when heated. The apparatus* was completely immersed in a quantity of the liquid to be examined, which thus filled the capillary tube.

Measurements were made of the heat dissipation associated with various small temperature excesses of the wire, ranging from 1° or 2° C. to 20° C. For this the Kelvin bridge was used in the manner already described. However, since only slight heating was used, the initial current was reduced to 0.01 ampere so that its heating effect should be negligible in these new conditions. The currents used for heating ranged up to about 1 ampere.

Thermal conductivities were calculated on the assumption of radial flow of heat between the wire and the inner surface of the silver tube. For moderate heating results so calculated increased as the temperature excess was raised, showing that convection currents had become appreciable. For slight heating, however, results were practically constant. The conductivity given in the tables is the value to which results tended as the temperature excess was reduced to zero.

The experiments were carried out with the liquids at two temperatures, about 20° C. and 80° C. respectively. No allowance was made for end effects, but probably the length of wire used (12.7 cm.) was sufficient to render these of little importance.

(e) *The ratio ($k/c\nu$).*

On the kinetic theory of gases the thermal diffusivity (k/c) bears a ratio to the kinematical viscosity $\dagger$ (ν), which is constant for a given kind of gas, and depends upon the number of atoms in a molecule. For liquids, owing to complexity of structure, such constancy does not hold, and a wide range of value is covered. It is to be expected on general grounds that this fundamental ratio between the factors determining the fluid flow and the heat transfer will be important in determining the cooling power of fluid streams. Consequently, for each of the liquids, $k/c\nu$ has been evaluated for a series of temperatures. It is the factor determining the complexity of a fluid when thermal and viscous actions are involved together, *i. e.* in convection of heat.

* This apparatus was available, having been constructed previously by Dr. Ezer Griffiths.

$\dagger$ Diffusivity of momentum.

5. THE WIRES USED.

The wires used were of specially pure platinum, and were of three sizes, being about 4, 6, and 8 mils* in diameter. Mean details are given in Table III.

TABLE III.

Details of the Wire used.

Total length between current terminals = 6.08 cm.
 Mean length between potential leads = l cm.
 Resistance per unit length at 0° C. = R_0/l ohms per cm.

Wire.	Diam.	l .	R_0/l .	α .
4 mil	0.0102 cm.	4.8	0.118	0.00386
6 mil	0.0152	*4.75	0.0564	0.00380
8 mil	0.0204	4.98	0.0294	0.00387

* Lengths 3.15 and 6.08 cm. were used in the end correction test.

Potential leads of 4 mil platinum wire were welded to the test wire at a distance from its ends. The length of wire between these leads was easily measured. Diameters were measured by means of a micrometer screw gauge reading to one ten thousandth part of an inch.

Before the wires were cut up into lengths for mounting in the holder of the rotating arm, temperature coefficients of resistance were determined for annealed samples. Lengths of about 30 cm. were used, and resistances were determined at the temperatures of melting ice, and of the vapour of water boiling under normal atmospheric pressure. Sulphur points had previously been determined. For these measurements use was made of a Callendar and Griffiths resistance bridge reading to 0.0001 ohm. However, in one case, using the Kelvin bridge arrangement, a check measurement was obtained for a portion of wire mounted in the normal manner in the holder of the whirling arm. The wire was immersed in a stirred oil bath at a few fairly steady temperatures, and the temperature coefficient of resistance thus obtained agreed to within 2 per cent. with the more accurate determination previously made.

During cooling experiments with the arm rotating, the finer wires tended to stretch slightly, presumably owing to

* 1 mil = 0.001 inch.

the strains set up. This was most readily detected by the change in resistance of the wire at $0^{\circ}\text{C}.$, a quantity which was regularly calculated from the measured resistance at the temperature of the oil. Necessary allowances for such changes were made in the heat-loss calculations. The effect, however, was slight, and in the whole life of a wire did not amount to more than 1 per cent. increase in length.

Throughout the experiments care was taken to keep the wire bright and free from adherent fluff, etc. If by accident it was over-heated, it became blackened with carbonized oil. On these occasions the wire was removed from the liquid, and the deposit was burnt off by heating the wire electrically to a dull redness. Naturally, after this procedure, particular attention was paid to alterations in resistance.

(i.) *Calculation of the heat-loss from the wire.*

The heat-loss from the wire during an experiment was calculated from the current " i " flowing through it, and from its hot resistance R , as measured on the Kelvin bridge. Results were converted from watts to calories per second, using 4.184 as the conversion factor. They were expressed in the form of heat-loss per cm. length per degree temperature elevation.

(ii.) *Calculation of the temperature excess of the wire.*

The temperature excess of the wire was calculated from the increment of resistance dR : on the platinum scale it is given by $\theta = dR/R_0\alpha$, where R_0 is the resistance of the wire at $0^{\circ}\text{C}.$, and α is the temperature coefficient of resistance. Corrections to the centigrade scale involve increasing the above value by about 1 per cent. for values of θ up to $20^{\circ}\text{C}.$ and by $1/5$ per cent. for $\theta = 60^{\circ}\text{C}.$ Such corrections are almost negligible, being greatest for the low values of θ , where the experimental errors were greatest. They may be obtained conveniently from tables showing the relation between the two scales*.

(iii.) *Correction due to radial temperature gradient in the wire.*

There is also a small correction due to the fact that, through its immediate proximity to the liquid, the surface of the wire becomes slightly cooler than the core. Calculation on certain assumptions shows the temperature difference

* Harker, Phil. Trans. A. cciii. p. 343 (1904).

between the core of the wire and its surface to be proportional to the rate of surface cooling*. In the notation of this paper it is given by $H\theta/4\pi K$, where K ($=0.166$ cal. per cm. per degree) is the thermal conductivity of the platinum of which the wire is composed. The mean temperature of the wire as obtained by resistance measurements is thus in excess of the surface temperature by an amount $d\theta$ given by $d\theta/\theta = H/8\pi K = 0.24 H$. From the tables of H , given later, we find that for water the relative error $d\theta/\theta$ is appreciable only for the highest speeds, and that for all other liquids it is invariably less than 1/3 per cent. No correction for this effect has therefore been made.

(iv.) *Correction for conduction by the potential leads and terminals.*

The wire was clamped to the holder by two terminals about 6.1 cm. apart, and the potential leads (4 mil) were attached at about $\frac{1}{2}$ cm. from the clamped ends. It was considered that at this distance the terminals would have no cooling effect on the test portion of the wire, and that the potential leads were sufficiently thin to be negligible in this respect.

If the terminals exert any appreciable cooling, measured heat-losses should depend upon the distance of the potential leads from the ends. With the liquids no such dependence was found. Direct test with oil No. 1 gave practically identical results, whether the potential leads were attached to the wire at the clamping terminals, at $\frac{1}{2}$ cm. from them, or at double this distance. Even with air as the fluid (where end cooling would be of much greater relative importance owing to the much smaller rates of surface cooling) differences were not very systematic and were limited to ± 5 per cent.†

It was inferred from these experiments that the heat lost by conduction to the terminals and potential leads was negligible in comparison with that carried off by the liquid streams.

6. RESULTS.

(i.) *Tables and Curves showing heat-losses obtained with each of the liquids.*

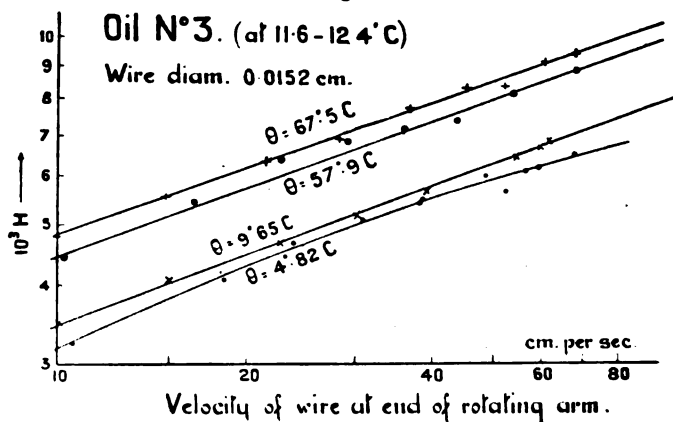
The results obtained in the experimental work were expressed in terms of the heat-loss H per centimetre length of wire per degree centigrade temperature excess. Observations were taken for various velocities of rotation, and for a series of values of temperature excess.

* King, *loc. cit.*

† Greatest values were indicated when the potential leads were attached at the extreme ends of the wires.

To present results in convenient comparative tables, it was necessary to obtain by interpolation values appropriate to certain selected velocities and temperatures. In this connexion a graph is given, fig. 5, which shows experimental points obtained for one of the oils, and the smooth curves from which representative results were read off. As regards

Fig. 5.



Specimen Experimental Results.

temperature excess, it will be seen that the values deviated but slightly from a convenient series, viz. 5° , 10° , 60° , and 70°C . The small adjustments necessary to give heat-losses corresponding to these exact values were obtained by further curves. The procedure with this oil is typical.

Tables IV. (i.–v.) give results compiled in the above

TABLE IV.—Heat losses ($10^5 H$) from Wires in Liquid Streams.

(H = calories per cm. per sec. per $^\circ\text{C}$. temperature excess of wire.)

(i.) Distilled Water *.							
Diameter of Wire.	Mean temperature of water.	Temperature excess of Wire.	$10^5 H$. For values of relative velocity (cm. per sec.).				
			10.	20.	40.	60.	70.
cm. 0.0204	° C. 11	° C. 8	2070	2900	4060	4950	5340
		20	2200	3090	4300	5250	5650
		35	2560	3460	4800	5830	6300

* Worthington and Malon give a value $10^5 H = 2960$, when $d = 0.0256\text{ cm.}$, $\theta = 30^\circ\text{C.}$, and $v = 14.85\text{ cm. per sec.}$ Frankl. Inst. J. 184. p. 115, 1917.

Table IV. (continued).

(ii.) Paraffin Oil.							
Diameter of Wire.	Mean temperature of oil.	Temperature excess of Wire.	10 ⁵ H. For values of relative velocity (cm. per sec.).				
			10.	20.	40.	60.	70.
cm.	° C.	° C.					
0.0152	17.6	5	460	622	840	993	1055
		50	487	677	940	1140	1230
0.0204	11	5	500	697	978	1190	1280
		50	572	798	1110	1350	1455

(iii.) Transformer Oil No. 1.							
0.0152	16	5	384	515	693	825	875
		10	400	532	705	827	880
		20	428	570	757	890	950
		40	450	603	795	944	1010
		60	467	625	835	1000	1068
0.0204	15	5	480	644	855	1014	1076
		10 †	483	646	863	1024	1095
		20	505	684	910	1070	1138
		40	550	745	990	1160	1237
		60 ‡	588	786	1040	1225	1305

(iv.) Transformer Oil No. 2.							
0.0102	11	5	315	425	553	630	660
		50	383	512	688	814	870
0.0152	11	5	358	468	610	713	758
		10	382	492	650	765	812
		20	395	520	687	808	860
		40	430	565	740	870	923
		60	458	598	778	906	960
0.0204	14	5	440	578	760	890	944
		50	542	727	972	1155	1230

(v.) Transformer Oil No. 3.							
0.0152	12	5	335	450	568	640	660
		10	363	468	600	695	737
		60	474	600	765	880	930
0.0204	16	5	406	535	702	825	877
		10	417	548	720	847	900
		20	468	612	800	940	1000
		40	512	672	890	1050	1118
		60	560	738	970	1140	1210

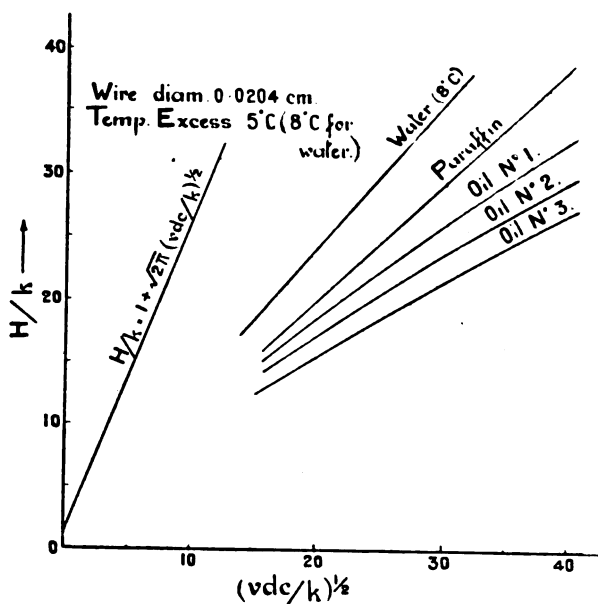
† A series at 10° C. excess taken much earlier and with a different wire gave smoothed results indistinguishable from these at the lower velocities, and falling to about 3 per cent. lower at 70 cm. per sec.

‡ An earlier series at 60° C. with a different wire gave smoothed values indistinguishable from these.

manner, and the values given bear a very close relation to actual points obtained in the experimental work. They present in some 200 orderly values the results of four or five times this number of observations.

A trial was made of representing these results on graphs in which heat-loss was plotted as ordinate against the square root of the velocity as abscissa. In general, the lines obtained were slightly curved, so that the results could not be conveniently expressed by a formula similar to that found

Fig. 6.



Results for Viscous Liquids compared with formula for Inviscid Fluids.

for gases (equation 2). Fig. 6 shows a series of results plotted on a graph of this form.

On plotting logarithmically, however, excellent straight lines were usually obtained, and results were studied from this point of view. Fig. 7 shows families of curves obtained for each of the liquids used. It is immediately evident that for a given liquid the lines are practically parallel, the slope having no marked dependence upon the diameter of the wire or upon its temperature excess. There is possibly a tendency

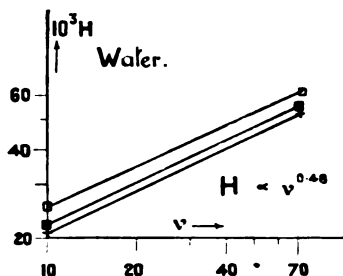
for the slope to be greater for the larger wires, but otherwise occasional irregularity of slope or of curvature appears to be

Fig. 7.

HEAT LOSS - VELOCITY CURVES.

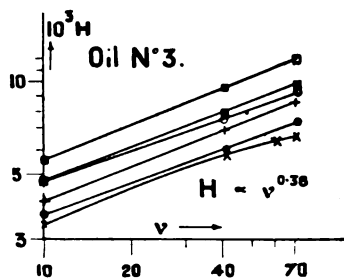
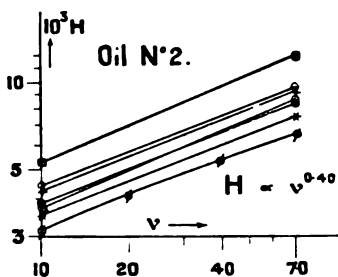
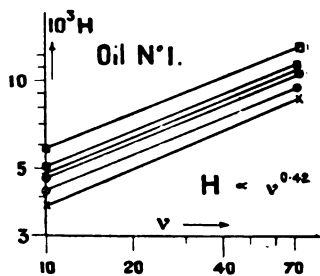
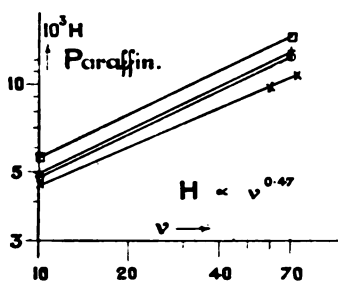
H = Heat loss per cm per degree Temperature excess. (calories)

v = Velocity of wire relative to fluid. (cm. per sec.)



Key

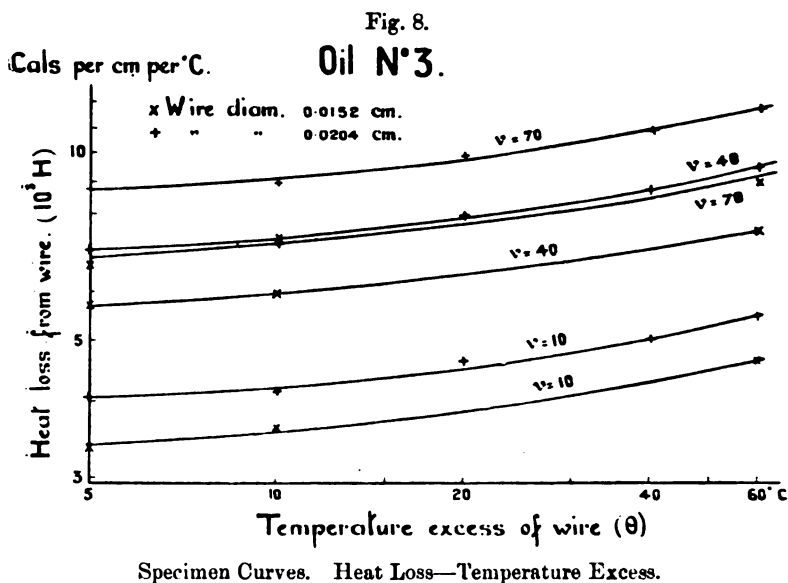
Wire diam cm.	Temp: excess θ		
	Low	Med.	High
0 0102	ϕ		ϕ
0 0152	x	$\bullet$	$\circ$
0 0204	+	$\blacksquare$	$\square$



due to experimental error, for with different liquids it is not associated consistently with any particular set of conditions.

Parallel lines are also obtained on plotting results with temperature excess (θ) as abscissa. This may be seen from

the curves shown in fig. 8. Thus the effect of temperature is to introduce a factor dependent only upon the nature of the liquid used.



(ii.) *Empirical relations.*

If we accept the families of curves of figs. 7 and 8 to be parallel lines, rectilinear in the former case, we find the following general formula covers the results:—

$$H = Mr^n(1 + a\theta + b\theta^2), \quad \dots \dots (9)$$

where n , a , and b depend only upon the liquid used, while M depends also upon the diameter of the wire.

The values of " a " and " b " are given later in Table V. Undoubtedly they are intimately connected with the rate at which the physical properties of the fluids vary with temperature. Since our theoretical formulæ are restricted to cases where the physical properties remain constant, discussion will be devoted mainly to cases where the temperature excess " θ " is so small that changes in the properties of the fluids are inappreciable. In these circumstances equation (9) becomes

$$H = Mr^n. \quad \dots \dots (10)$$

Trial of a more general relation of the form *

$$H/k = N(vdc/250k)^n$$

showed N to depend upon both vdc/k and k/cv , so that the effects of these two terms are inter-related. While in the present experiments " n " exhibits no appreciable variation with vdc/k , being given by

$$n \text{ varies as } (k/cv)^{0.03-0.04}, \dots (11)$$

published values for gases cover a much wider range and indicate that

$$n \text{ varies as } (vdc/k)^{0.066}, \dots (12)$$

Now to a certain degree of approximation equations (11) and (12) can be combined in the form

$$n \text{ varies as } \{(vdc/k) \times (k/cv)^{\frac{1}{2}}\}^{0.066}, \dots (13)$$

and it was decided to test whether the new variable thus revealed would express completely the inter-relation of (vdc/k and k/cv).

(iii.) *Formula covering all results.*

It was then found possible to express our experimental results in a formula of the type

$$H/k = A \cdot B \cdot C \cdot F \{(vdc/k) \times (k/cv)^{\frac{1}{2}}\}^{\dagger}, \dots (14)$$

where $A (= 1 + a\theta + b\theta^2)$ depends upon the temperature excess of the wire and the nature of the fluid, and is undoubtedly connected with the rate at which the physical properties of the fluid vary with temperature.

B represents a small residual effect of wire diameter, additional to that covered by the " vd " term. It depends somewhat upon the nature of the liquid.

$C [= f(k/cv)]$ is dependent only upon the nature of the fluid. It varies as $(k/cv)^{-m}$, where $m=0$ for gases and increases to about 0.19 in the region of the viscous oils.

* In the experiments the minimum value of vdc/k for each liquid was about 250. By writing $vdc/250k$ instead of vdc/k the advantage is gained that N has a definite physical meaning. It is the lowest value of H/k actually measured, instead of being the extrapolated value associated with $vdc/k=1$.

† $\{(vdc/k) \times (k/cv)^{\frac{1}{2}}\} = \{(vdc/k) \times (vd/\nu)\}^{\frac{1}{2}} = \{(vd/\nu) \div (k/cv)\}^{\frac{1}{2}}$.

The formula is of the general form expected (3), except for the small corrections represented by the terms A and B. The particular grouping of variables within the brackets correlates the various slopes of the lines in fig. 7 with the curvature observed when study is made of an extended vdc/k curve for gases.

TABLE V.
Values of A and B.

$A = 1 + a\theta + b\theta^2$, where θ = temperature excess of wire.

Fluid.	10^3a .	10^3b .	Values of B		
			For wire diam. cm.		
			0.0102	0.0152	0.0204
(Air)*	...	...	(0.91-0.94)	(0.95-0.97)	1
Water	2.64	12	...	...	1
Paraffin	2.94†	...	...	0.98	1
Oil No. 1	7.25	-5.08	...	0.92	1
Oil No. 2	10.7	-8.42	0.93	0.90	1
Oil No. 3	13.5	-9.52	..	0.90	1

* Calculated from King's results.

† Mean value obtained from results at temperature excesses 5° C. and 50° C.

TABLE VI.
Relation between C and k/cv .

k/cv .	cv/k .	C.
1	1	1.02
0.1	10	1.17
0.01	100	1.46
0.001	1000	1.98

(a) *The dependence of A upon temperature variations in the physical properties of the liquid.*

The physical property of the liquid which depended most upon temperature was the viscosity. In some cases the cold oil was as much as ten times as viscous as hot oil at the

temperature of the wire. Such variations may be too great to be covered by a simple correction applied to a theoretical formula based upon assumptions of constancy. The temperature effect has therefore been left in the empirical form given above, k , c , and v having the values appropriate to the cold fluid.

It is worth notice, however, that the effect is generally rather greater than can be allowed for in the final formula by supposing the physical properties of the fluid to be those appropriate even to the temperature of the hot wire. Generally, for 60° C. temperature excess of the wire, about 10 per cent. increment in heat-loss has still to be accounted for.

(b) *Variation of B with wire diameter.*

By plotting curves showing the relation between H and vd , and noticing the factors B necessary to bring the curves for the finer wires into coincidence with the curves for the stouter, the values given in Table V. were obtained. The total range in the value of B , about 10 per cent., is too small for deducing the laws governing its variations, but a definite diameter effect is indicated. The order of the effect found for liquids is seen to be the same as that for air as calculated from King's formula. Special experiments with the present apparatus, on the air-cooling of the 6 mil and 8 mil wires, gave ratios of heat-loss in good agreement with King's values*. This eliminates experimental error as an explanation of the differences found for these wires when liquids were used.

Considerations of the theory of dimensions show that, in the theoretical formula, wire diameter and velocity must always occur together, unless variables are involved additional to those included above. If free convection effects are included the variable ag may be introduced, where α =volume coefficient of expansion of the fluid and g =acceleration due to gravity. A term $cgd^3\alpha\theta/kv$ † (or its equivalent), found by the author to cover free convective cooling

* Results were not corrected for swirl, but comparisons were made at definite arm velocities. The actual magnitudes of heat-loss were almost identical with those calculated from King's formula, provided the swirl velocity in the trough was about 12 per cent. of the arm velocity. Such a figure is reasonable since values of 10 per cent. to 20 per cent. were obtained when liquids were used. King found a 5 per cent. swirl in a large room.

† If, in addition to the free convection variables, the density of the fluid is also separately introduced [it is already included to some extent in $c(=\rho)$ and $v(=\eta/\rho)$] a term results which contains d without either θ or v . Richardson has discussed the relation borne by such a term to King's results (Phys. Soc. Proc. xxxii. p. 405, 1920).

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in viscous liquids, may then be expected in the complete equation. If B owes its origin to this new correction term, its dependence (Table V.) upon the nature of the liquid (ca/kv) is thus explained. Some associated dependence upon the temperature excess θ is also to be expected, and this may explain the residual relation between A and θ not previously accounted for. It may also explain why, in King's results, his diameter term is associated with a residual θ term much larger than that which operates upon the velocity group.

While the term B may have its origin in natural convection effects, other possibilities must not be overlooked. As previously stated, the diameter effect indicated by Hughes's results for large cylinders is in the opposite sense to that found in the present experiments with fine wires. The distribution of heat flux across the boundary may have been different in this case.

(c) *Relation between C and the nature of the liquid.*

$$C = f(k/cv) \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Fig. 9 shows the manner in which C depends upon the value of k/cv for the liquid used. It was obtained for the 8 mil wire and for small values of temperature excess by plotting H/k as ordinate against $\{vdc/k \times (k/cv)^{\frac{1}{2}}\}$ as abscissa. A series of curves was thus obtained parallel to neighbouring portions of the extended curve for air, but displaced by amounts depending upon the nature of the liquid used. Measurement was made of the amounts of displacement, that is, of the factors C necessary to bring all the curves into coincidence with that for air. It is seen that a smooth relation is indicated between C and k/cv . Values read off from fig. 9 are given in Table VI.

(d) *Curve showing correlation effected.*

Fig. 10 has been drawn to show the extent to which the final formula (14) represents the results of the experimental work. Ordinates give the value of $[H/k] + [A.B.C]$ and abscissæ represent $[vdc/k \times (k/cv)^{\frac{1}{2}}]$. Values taken for A, B, and C are those given above.

The points shown represent the experimental values for liquids as given in Tables IV. (i.-v.). For convenience only a selected number of points have been plotted, and these refer

only to small temperature excesses, but each wire is represented by high (70 cm. per sec.) and low (10 cm. per sec.) velocities for each of the liquids used.

Fig. 9.

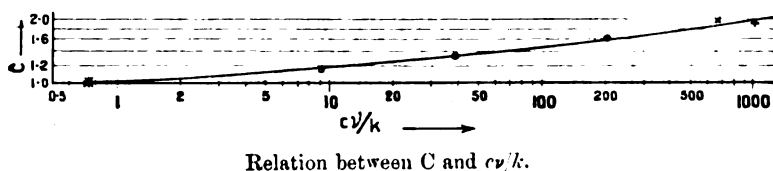
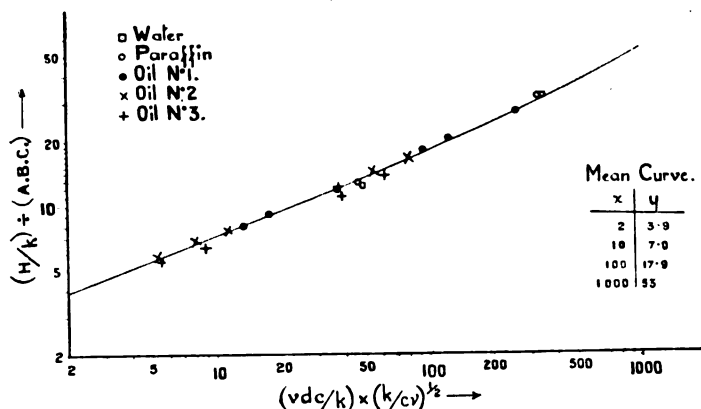


Fig. 10.



Representative Results for all Fluids plotted on one curve.

The line drawn is part of the mean curve* for gases referred to earlier, re-drawn on the present basis, taking for air $k/cv=1.35$ †. In the region shown, $H/k.A.B.C.$ varies as $[vdc/k \times (k/cv)^{1/2}]^n$, where n varies from 0.38 to 0.48.

* The curve is the mean for gases obtained by the method described elsewhere. No correction terms in B or in $(1+a\theta+b\theta^2)$ have been used, but temperature changes in the properties of air have been approximately allowed for by taking values of k , c , and v for temperatures intermediate between that of the cold air and that of the hot wire. Little difference in the mean curve is obtained if the constants are evaluated for a temperature equal to that of the hot wire.

† c refers to unit volume and constant pressure. If the constant volume value is taken, a slight alteration in the form of the function f is all that is necessary to give a curve practically as good as the present one. All values of $f(x)$ for x greater than 9 have to be reduced by 30 per cent. and the alteration in $f(x)$ for lower values of x falls to zero as x approaches 1.90, the new value of k/cv for air.

The figure shows that equation (14) satisfactorily represents our results. It is as far as possible of the type suggested by theoretical considerations, but is empirical as regards the actual form of the functions given.

I desire to express my thanks to Dr. G. W. C. Kaye, Superintendent of the Physics Department of the National Physical Laboratory, for the helpful manner in which all the facilities for the work have been provided. Mr. R. R. Strand, Senior Observer, helped with the constructional work and rendered very valuable assistance with the experimental observations.

January 1924.

CV. *Note on the Auto-Transformer and on the Impedance as a Tensor.* By W. H. INGRAM, M.Sc.*

SYNOPSIS.—A formula is given for the voltage at a tap in the primary of a transformer, and it is shown that under given conditions this voltage will be independent of the load on the transformer.

Impedance is defined as a tensor.

IN a recently published note † I gave a voltage formula for the step-down auto-transformer which showed that the secondary terminal voltage will be independent of the exciting current when a certain ratio is obtained between the self-impedances of the two windings into which the auto-transformer is divided by the tap. A similar phenomenon may be exhibited in the case of a transformer having a tapped primary or, which is the same thing, a step-down auto-transformer having a (metallically independent) tertiary.

Let the auto-transformer be the one specified in the above-mentioned Note, and the tertiary have n_3 effective turns. The working flux, or the flux that links the windings n_1 , n_2 , and n_3 perfectly, is to be imagined as also linking the winding n_0 of the imaginary core-impedance circuit. The system n_1 , n_2 , n_3 , and n_0 represents an ideal voltage transformer, giving the first of the following relations, the next two being given by the usual current and m.m.f. conditions:

$$\left. \begin{aligned} e_1/n_1 &= e_2/n_2 \text{ etc.}, \\ i_1 &= i_2 + i_a, \\ n_1 i_1 + n_2 i_2 + n_3 i_3 &= n_0 i_0. \end{aligned} \right\} \dots \dots \dots (1)$$

* Communicated by the Author.

† Phil. Mag. xlvii. p. 241 (Jan. 1924).

Applying the usual circuital work theorem :

$$\left. \begin{aligned} E_1 &= e_1 + Z_1 i_1 + Z_{12} i_2 + Z_{13} i_3 + E_a, \\ E_a &= e_2 + Z_2 i_2 + Z_{21} i_1 + Z_{23} i_3, \end{aligned} \right\} \dots (2)$$

where E_1 is the voltage impressed on the transformer primary ; E_a the auto-transformer secondary voltage ; i_3 the current in the n_3 winding ; Z_1 the self-impedance of the winding 1 (the reactance of which is due to the leakage flux exclusively associated with this winding, and the resistance of which is made up of the ohmic resistance of the conductor plus small in-phase effects due to eddys, etc.) ; and Z_{13} , for instance, the mutual impedance between the windings 1 and 3, the reactive part of which is due to flux linkages between the two coils denoted by the subscripts. Solving for E_a in terms of the impressed voltage E_1 , the delivered currents i_a and i_3 , and the exciting current i_0 :

$$\begin{aligned} E_a = \frac{n_2}{n_1 + n_2} E_1 - n_0 & \left(\frac{n_2 Z_1 - n_1 Z_2}{(n_1 + n_2)^2} + \frac{n_2 Z_{12} - n_1 Z_{21}}{(n_1 + n_2)^2} \right) i_0 \\ & - \left[\frac{n_1^2 Z_2 + n_2^2 Z_1}{(n_1 + n_2)^2} - n_1 n_2 \frac{Z_{21} + Z_{12}}{(n_1 + n_2)^2} \right] i_a \\ & - \left[n_3 \frac{n_2 Z_1 - n_1 Z_2}{(n_1 + n_2)^2} + n_3 \frac{n_2 Z_{12} - n_1 Z_{21}}{(n_1 + n_2)^2} \right. \\ & \quad \left. - \frac{n_2 Z_{13} - n_1 Z_{23}}{(n_1 + n_2)} \right] i_3 * \dots (4) \end{aligned}$$

The coefficient of i_3 simplifies somewhat from the fact that $Z_{13} : Z_{23} \sim M_{13} : M_{23} = n_1 : n_2$ (since the paths of all the stray fluxes in any actual iron-cored transformer are mainly iron-free, $Z_{13} i_3$ is practically equal to $M_{13} di_3/dt$, numerically). The impedances Z_{12} , Z_{31} (equal) have no significance, and should be omitted in any case where there is no tertiary winding, as it is here introduced merely to take care of the flux that links the windings 1 and 2 but not 3, which flux is to be considered as part of the working flux when there is no tertiary.

From the fact that Z_1 and Z_2 may represent the self-impedances *plus* any external impedances that may be introduced in series with the windings 1 and 2 respectively,

* The sign of i_3 here is taken to conform with the actual direction of the current. Formula (4) also applies when the winding n_3 is an auto-transformer booster winding ; when the tertiary is connected as a negative booster, the sign of n_3 is to be reversed.

it is clear that by a manipulation of these latter impedances the coefficient of i_3 may be reduced to null. The line and generator impedances may also be included in Z_1 , in which case E_1 becomes the internal e.m.f. of the generator.

The present opportunity seems not inappropriate to point out that impedances are *tensors*, and when defined as such enable us to put the "symbolic" method on a purely vector basis. The imaginary number unit occurring in the usual $Z = R + \sqrt{-1}X$ is entirely devoid of any physical significance, serving merely to establish a certain orthogonality, and has a further disadvantage in that the coordinate system must be adjusted to every i upon which Z operates.

The tensor components of Z may be obtained from the work theorem for the most general simple circuit having lumped constants :

$$E = Ri + L \frac{di}{dt} + \frac{1}{c} \int i dt. \quad . \quad . \quad . \quad (5)$$

If g_1 be a unit vector in the reference-line (see the first paragraph of the above-mentioned Note) we have :

$$\left. \begin{aligned} i \cdot g_1 &= i_{\max} \cos(i, g_1) = i, \\ E \cdot g_1 &= E, \end{aligned} \right\} \quad . \quad . \quad . \quad (6)$$

which may be substituted in (5), giving :

$$E = \left[R + \left(L\omega - \frac{1}{\omega C} \right) \omega_1 \times \right] i = [R + X \omega_1 \times] i, \quad . \quad (7)$$

where ω_1 is a unit vector perpendicular to the plane containing i and g_1 , ω the angular velocity of the vector E . In obtaining (7) the relations

$$\frac{di}{dt} = \omega \times i, \quad \int i dt = \frac{-1}{\omega} \omega_1 \times i \quad . \quad . \quad . \quad (8)$$

are made use of, the first of which is obtained directly from elementary vector considerations, and the second by an "educated guess" and verified by differentiation.

An n -fold iteration of Z is written Z^n , and from geometrical considerations is a tensor that rotates n times the angle Z does and stretches to the n th power of the stretch of Z . The reciprocal tensor Z^{-1} is equal to Z_c/Z^2 , where Z_c is the conjugate $(R - X \omega_1 \times)$ of Z , and $Z^2 = R^2 + X^2$. The distributive law and the commutative and associative laws of addition and multiplication for operator and operand are the same as for

algebraic quantities, except the commutative law of multiplication for the operand : $\mathbf{Za} \cdot \mathbf{b} = \mathbf{Zc} \cdot \mathbf{a}$; hence $\mathbf{Z}$ may be said to be skew-symmetric. Such dot products occur in calculating wattages ; for example, the average power-loss in excitation of a transformer over a cycle is $\bar{w} = \frac{1}{2} \Sigma \mathbf{e}_j \cdot \mathbf{i}_0$, where the $\mathbf{e}_j$'s are internal e.m.f.'s (but not counter e.m.f.'s appearing anywhere as driving forces). Writing $\Sigma \mathbf{e}_j = \mathbf{Z}_0 \mathbf{i}_0$, ($n_0 = \Sigma n_j$) gives $\bar{w} = \frac{1}{2} \mathbf{R}_0 i_0^2$. Another expression for $\bar{w}$ is obtainable from $\mathbf{e}_j = n_j d\phi/dt$; hence, using (8), $\bar{w} = \frac{1}{2} \Sigma n_j \Phi \times \mathbf{i}_0 \cdot \boldsymbol{\omega}$, showing that the component of $\mathbf{i}_0$ in phase with ϕ is wattless.

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CVI. *The Approximate Solution of Two-Dimensional Problems in Elasticity.* By Prof. S. TIMOSCHENKO, *Research Dept., Westinghouse El., E. Pittsburgh, Pa.**

§ 1. **I**N two-dimensional systems of stress generated by corresponding boundary forces, the three stress-components at any point can be deduced from a single function ϕ , which satisfies the equation

$$\nabla^4 \phi = 0. \quad \dots \dots \dots (1)$$

The solution of (1), in conjunction with specified boundary conditions, is not always an easy matter. The object of this paper is to outline an approximate method for investigating the two-dimensional problem by using the expression for the potential energy †, viz. :

$$V = \frac{1}{2E} \iint (X_x^2 + Y_y^2 - 2\sigma X_x Y_y + 2(1 + \sigma) X_y^2) dx dy. \quad (2)$$

We assume that the stress-function can be represented by the series

$$\phi = \phi_0 + \alpha_1 \phi_1 + \alpha_2 \phi_2 + \alpha_3 \phi_3 + \dots, \quad \dots \dots (3)$$

where $\phi_0, \phi_1, \dots$ are functions specified in such a manner as to correspond to the given boundary conditions.

The three stress-components will be

$$\left. \begin{aligned} X_x &= \frac{d^2 \phi}{dy^2} = \phi_{0yy} + \Sigma \alpha_n \phi_{nyy}, \\ Y_y &= \frac{d^2 \phi}{dx^2} = \phi_{0xx} + \Sigma \alpha_n \phi_{nxx}, \\ X_y &= -\frac{d^2 \phi}{dx dy} = -\phi_{0xy} - \Sigma \alpha_n \phi_{nxy}. \end{aligned} \right\} \quad \dots \dots (4)$$

* Communicated by the Author.

† The method was used by the author for calculating the stress-distribution in a compressed block. See his 'Treatise on Elasticity,' vol. i. p. 143 (St. Petersburg, 1914). [Russian.]

If we substitute these expressions in (2), we obtain the energy function V as a quadratic function of the coefficients $\alpha_1, \alpha_2, \dots$

By variation of these coefficients we obtain

$$\delta V = \int (\delta X_v u + \delta Y_v v) ds, \quad (5)$$

where $\delta X_v, \delta Y_v$ are the corresponding variations of boundary tensions, and u, v are the boundary displacements.

When the right side of (5) is equal to zero, we obtain

$$\delta V = 0. (6)$$

To obtain an approximate solution of any problem, we take a few terms in the series (3), and, using the conditions (6), determine the coefficients $\alpha_1, \alpha_2, \dots$ from the linear equations

$$\frac{dV}{d\alpha_1} = 0, \quad \frac{dV}{d\alpha_2} = 0, \quad (7)$$

Making use of (2) and (4), we may write these equations as follows :

$$\iint \{ (\phi_{0yy} + \Sigma \alpha_m \phi_{myy}) \phi_{nyy} + (\phi_{0xx} + \Sigma \alpha_m \phi_{mxx}) \phi_{nxx} \\ - \sigma (\phi_{0yy} + \Sigma \alpha_m \phi_{myy}) \phi_{nxx} - \sigma (\phi_{0xx} + \Sigma \alpha_m \phi_{mxx}) \phi_{nyy} \\ + 2(1 + \sigma) (\phi_{0xy} + \Sigma \alpha_m \phi_{mxy}) \phi_{nxy} \} dx dy = 0. \quad (8)$$

In many cases the stress-distribution is independent of the elastic constants. We can then put $\sigma=0$, and replace equation (8) by a simpler equation as follows :

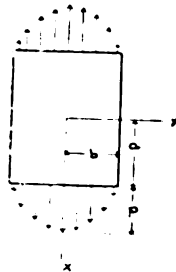
$$\iint \{ (\phi_{0yy} + \Sigma \alpha_m \phi_{myy}) \phi_{nyy} + (\phi_{0xx} + \Sigma \alpha_m \phi_{mxx}) \phi_{nxx} \\ + 2(\phi_{0xy} + \Sigma \alpha_m \phi_{mxy}) \phi_{nxy} \} dx dy = 0, \quad (8)'$$

§ 2. As a first example of the method outlined, we proceed to consider the stress-distribution in a rectangular plate (fig. 1), on the edges ($x = \pm a$) of which known normal tractions act.

We choose the function ϕ_0 in such a manner as to satisfy the boundary conditions. The functions $\phi_1, \phi_2, \dots$ we take in such a form that the corresponding stresses vanish at the boundary.

For example, in the case of a parabolic distribution of tensile tractions on the edges $x = \pm a$ we may assume a

Fig. 1.



stress-function of the type :

$$\phi = \frac{1}{2} p y^2 \left(1 - \frac{1}{6} \frac{y^2}{b^2} \right) + (x^2 - a^2)^2 (y^2 - b^2)^2 (\alpha_1 + \alpha_2 x^2 + \alpha_3 y^2 + \dots). \quad (9)$$

To the first member of the expression corresponds the parabolic stress-distribution represented in fig. 2 by the curve I. If we take two first members of (9), we have to calculate the coefficient α_1 . Using in this case equation (8), we obtain

$$\alpha_1 \left(\frac{64}{7} + \frac{256}{49} \frac{b^2}{a^2} + \frac{64}{7} \frac{b^4}{a^4} \right) = \frac{p}{a^4 b^2}.$$

In the case of a square plate ($a=b$) we obtain

$$\alpha_1 = 0.04253 \frac{p}{a^6}.$$

The stress-components will be

$$X_x = p \left(1 - \frac{y^2}{a^2} \right) - 0.1702 p \left(1 - \frac{3y^2}{a^2} \right) \left(1 - \frac{x^2}{a^2} \right)^2,$$

$$Y_y = -0.1702 p \left(1 - \frac{3x^2}{a^2} \right) \left(1 - \frac{y^2}{a^2} \right)^2,$$

$$X_y = -0.6805 p \cdot \frac{xy}{a^2} \left(1 - \frac{x^2}{a^2} \right) \left(1 - \frac{y^2}{a^2} \right).$$

The corresponding distribution of stresses X_x on the cross-section $x=0$ is represented by the curve II. (fig. 2).

To obtain a closer approximation, we take the first four members of (9). Then the equations for the calculation of α_1 , α_2 , and α_3 will be

$$\left. \begin{aligned} \alpha_1 \left(\frac{64}{7} + \frac{256}{49} \frac{b^2}{a^2} + \frac{64}{7} \frac{b^4}{a^4} \right) + \alpha_2 a^2 \left(\frac{64}{77} + \frac{64}{49} \frac{b^4}{a^4} \right) + \alpha_3 a^2 \left(\frac{64}{49} \frac{b^2}{a^2} + \frac{64}{77} \frac{b^6}{a^6} \right) &= \frac{p}{a^4 b^2}, \\ \alpha_1 \left(\frac{64}{11} + \frac{64}{7} \frac{b^4}{a^4} \right) + \alpha_2 a^2 \left(\frac{192}{143} + \frac{256}{77} \frac{b^2}{a^2} + \frac{192}{7} \frac{b^4}{a^4} \right) + \alpha_3 a^2 \left(\frac{64}{77} \frac{b^2}{a^2} + \frac{64}{77} \frac{b^6}{a^6} \right) &= \frac{p}{a^4 b^2}, \\ \alpha_1 \left(\frac{64}{7} + \frac{64}{11} \frac{b^4}{a^4} \right) + \alpha_2 a^2 \left(\frac{64}{77} + \frac{64}{77} \frac{b^4}{a^4} \right) + \alpha_3 a^2 \left(\frac{192}{7} \frac{b^2}{a^2} + \frac{256}{77} \frac{b^4}{a^4} + \frac{192}{143} \frac{b^6}{a^6} \right) &= \frac{p}{a^4 b^2}. \end{aligned} \right\} (10)$$

In the case of a square plate we obtain

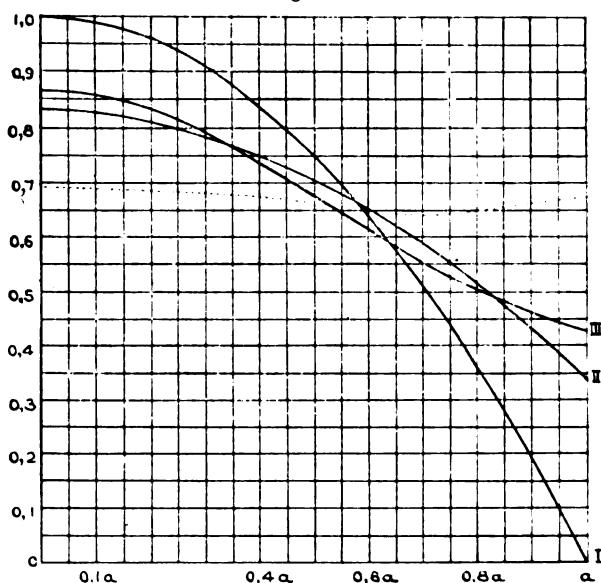
$$\alpha_1 = 0.04040 \frac{p}{a^6}; \quad \alpha_2 = \alpha_3 = 0.01174 \frac{p}{a^8}.$$

The stress-distribution on the cross-section $x=0$ will be given by

$$(X_x)_{x=0} = p \left(1 - \frac{y^2}{a^2} \right) - 0.1616 p \left(1 - \frac{3y^2}{a^2} \right) + 0.0235 \left(1 - 12 \frac{y^2}{a^2} + 15 \frac{y^4}{a^4} \right).$$

On fig. 2 it is represented by the curve III.*

Fig. 2.



With an increase in the length of the plate, the stress-distribution over the cross-section $x=0$ becomes more and more uniform. If we take for instance $a=2b$, we have from the equations (10)

$$\alpha_1 = 0.07983 \frac{p}{a^4 b^2}; \quad \alpha_2 = 0.1250 \frac{p}{a^6 b^2}; \quad \alpha_3 = 0.01826 \frac{p}{a^6 b^2}.$$

* Similar results were obtained by Prof. C. E. Inglis in the case of a sinusoidal distribution of tractions on the edges $x = \pm a$. See paper, "Two-dimensional Stresses in Rectangular Plates," read before Section G of the British Association at Edinburgh, September 1921.

The corresponding value of stresses on the cross-section ($x=0$) will be

$\frac{y}{a} =$	0	0.2	0.4	0.6	0.8	1.0
$(X_x)_{x=0} =$	0.690 p	0.684 p	0.669 p	0.653 p	0.649 p	0.675 p

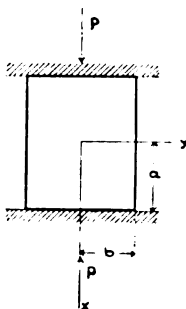
This distribution is represented on fig. 2 by a dotted line. We see that the deviation from the average stress (equal to $\frac{2}{3}p$) is now within the limits of accuracy of our approximate solution.

In the case of other symmetrical distributions of tractions over the edges $x = \pm a$ we have only to change the form of the function ϕ_0 in the expression (9): then the right-hand expressions only, in equations (10), have to be changed.

It is well known that if a thin plate, initially flat, be bent by couples and forces applied at its edges, the equation satisfied by the principal curvatures of its surface is mathematically identical with the equation (1)*. Hence, any solution of the two-dimensional problem can be used for investigating the bending of a thin plate with appropriate conditions at the boundary. The problem explained above corresponds to the bending of a rectangular plate, the deflexions (w) of which satisfy the following conditions at the boundary:

$$\left(\frac{dw}{dy}\right)_{y=\pm b} = \pm \frac{2}{3}pb; \quad \left(\frac{d^2w}{dy^2}\right)_{x=\pm a} = p\left(1 - \frac{y^2}{b^2}\right); \quad \left(\frac{dw}{dx}\right)_{x=\pm a} = 0.$$

Fig. 3.



§ 3. As a second example, we will consider the problem of a block between two perfectly rigid bearing-plates (fig. 3). We suppose that horizontal displacements on the contact surfaces are prevented by friction. The conditions on the free boundary of the block will be satisfied if

* This identity can be used in experimental solutions of two-dimensional problems. See K. Wieghardt, 'Mitteilungen u. Forschungsarbeiten,' H. 49 (1908).

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we take the stress-function in the form

$$\phi = -\frac{py^2}{2} + (y^2 - b^2)^2 (\alpha_1 + \alpha_2 x^2 + \alpha_3 x^4 + \alpha_4 x^2 y^2 + \dots), \quad (11)$$

where p denotes the value of the average compressive stress.

Limiting ourselves to the four terms in brackets, we obtain the following expressions for the stress-components:—

$$X_x = -p + (12y^2 - 4b^2)(\alpha_1 + \alpha_2 x^2 + \alpha_3 x^4) \\ + \alpha_4 x^2 (30y^4 - 24y^2 b^2 + 2b^4),$$

$$Y_y = 2(y^2 - b^2)^2 (\alpha_2 + 6\alpha_3 x^2 + \alpha_4 y^2),$$

$$X_y = -8y(y^2 - b^2)(\alpha_2 x + 2\alpha_3 x^3) - 4\alpha_4 x(3y^5 - 4y^3 b^2 + yb^4).$$

We see that, with the assumption made in regard to the displacements at the contact surfaces, the right side of (5) will be equal to zero. The stress-distribution in the case considered depends on the elastic constants, and we must take the equations for calculating the coefficients $\alpha_1, \alpha_2, \dots$ in the form (8). After performing the integrations, we obtain these equations in the following form:—

$$\left. \begin{aligned} \alpha_1 + \alpha_2 a^2 \left(\frac{1}{3} + \sigma \frac{4}{21} \frac{b^2}{a^2} \right) + \alpha_3 a^4 \left(\frac{1}{5} + \sigma \frac{8}{21} \frac{b^2}{a^2} \right) + \alpha_4 a^4 \frac{1}{21} \frac{b^2}{a^2} &= 0, \\ \alpha_1 \left(4 + \sigma \frac{16}{7} \frac{b^2}{a^2} \right) + \alpha_2 a^2 \left[\frac{12}{5} + \frac{32}{21} \frac{b^4}{a^4} + (2 + 3\sigma) \frac{32}{21} \frac{b^2}{a^2} \right] \\ + \alpha_3 a^4 \left[\frac{12}{7} + \frac{64}{21} \frac{b^4}{a^4} + \sigma \frac{112}{35} \frac{b^2}{a^2} + (1 + \sigma) \frac{128}{35} \frac{b^2}{a^2} \right] \\ + \alpha_4 a^4 \left(\frac{12}{35} \frac{b^2}{a^2} + \frac{32}{231} \frac{b^6}{a^6} \right) &= -\frac{\sigma p}{a^2}, \\ \alpha_1 \left(\frac{6}{5} + \sigma \frac{16}{7} \frac{b^2}{a^2} \right) + \alpha_2 a^2 \left[\frac{6}{7} + \frac{32}{21} \frac{b^4}{a^4} + \sigma \frac{8}{5} \frac{b^2}{a^2} + (1 + \sigma) \frac{64}{35} \frac{b^2}{a^2} \right] \\ + \alpha_3 a^4 \left[\frac{3}{2} + \frac{576}{105} \frac{b^4}{a^4} + \sigma \frac{96}{49} \frac{b^2}{a^2} + 2(1 + \sigma) \frac{64}{49} \frac{b^2}{a^2} \right] \\ + \alpha_4 a^4 \left[\frac{6}{49} \frac{b^2}{a^2} + \frac{32}{231} \frac{b^6}{a^6} \right] &= -\frac{\sigma p}{a^2}, \\ \alpha_1 \cdot 4 + \alpha_2 a^2 \left(\frac{12}{5} + \frac{32}{33} \frac{b^4}{a^4} \right) + \alpha_3 a^4 \left(\frac{12}{7} + \frac{64}{33} \frac{b^4}{a^4} \right) + \alpha_4 a^4 \left[\frac{36}{5} \frac{b^2}{a^2} \right. \\ + \left. \frac{32}{143} \frac{b^6}{a^6} + (2 + 3\sigma) \frac{32}{33} \frac{b^4}{a^4} \right] &= -\frac{\sigma p}{a^2}. \end{aligned} \right\} \quad (12)$$

We will make the calculations in the case of a square block.

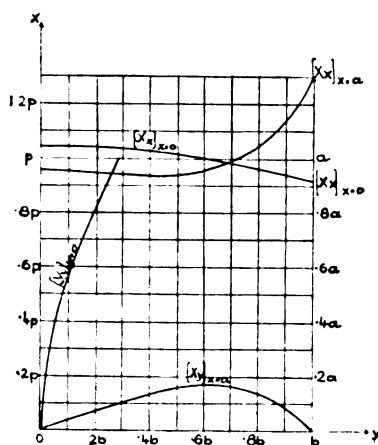
Putting $a=b$, $\sigma=\frac{1}{4}$, we get the following values of coefficients:

$$\begin{aligned}\alpha_1 &= 0.01016 \frac{p}{a^2}; & \alpha_2 &= -0.00629 \frac{p}{a^4}; \\ \alpha_3 &= -0.02336 \frac{p}{a^6}; & \alpha_4 &= -0.01825 \frac{p}{a^6}.\end{aligned}$$

The corresponding values of the stress-components on the contact surfaces and on the cross-sections ($x=0$) and ($y=0$) are given in the table below:

$\frac{x}{a} = \frac{y}{b} =$	0	0.2	0.4	0.6	0.8	0.9	1.0
$(X_x)_{x=\pm a} \dots$	-0.959 p	-0.951 p	-0.940 p	-0.956 p	-1.052 p	-1.152 p	-1.302 p
$(X_x)_{x=0} \dots$	-1.041 p	-1.033 p	-1.021 p	-0.997 p	-0.963 p	-0.942 p	-0.919 p
$(X_y)_{x=\pm a} \dots$	0	0.069 p	0.130 p	0.165 p	0.141 p	0.090 p	0
$(Y_y)_{y=0} \dots$	-0.013 p	-0.024 p	-0.057 p	-0.113 p	-0.192 p	-0.240 p	-0.292 p

Fig. 4.

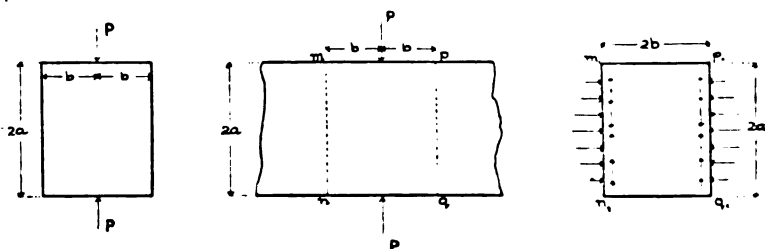


This stress-distribution is represented in fig. 4. We see that the compressive stresses are not distributed uniformly on the contact surfaces. There is some decrease of stress in

the middle, and a considerable increase near * the edges ($y = \pm b$). There are also tangential stresses acting on the contact surfaces. The maximum value of these is about 16 per cent. of the average compressive stress (fig. 4).

The block problem in the case of compression with two concentrated forces (fig. 5a) can be solved by combining the known solution for an infinite strip † (fig. 5b) with that for a block (fig. 5c), on the edges m_1n_1 and p_1q_1 of which

Fig. 5.



tractions corresponding to the stresses on the cross-sections mn and pq of the strip act. The last problem can be solved in the manner explained in the first example above.

§ 4. The same method can be used in order to estimate the additional deflexion of a beam due to shearing. The boundary conditions will be satisfied if we take the stress-function in the following form :

$$\phi = \alpha_1 \left[xy + \frac{1}{3c^2} (l-x)y^3 \right] + \alpha_2 e^{-\beta x} (y^2 - c^2)^2 y. \quad (13)$$

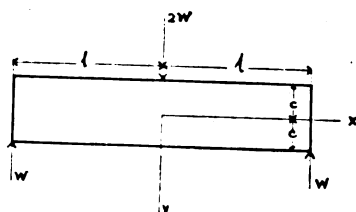
The corresponding stress-components will be

$$\left. \begin{aligned} X_x &= \frac{2\alpha_1}{c^2} (l-x)y + \alpha_2 e^{-\beta x} (20y^3 - 12c^2y), \\ Y_y &= \alpha_2 \beta^2 e^{-\beta x} (y^2 - c^2)^2 y, \\ X_y &= -\frac{\alpha_1}{c^2} (c^2 - y^2) + \alpha_2 \beta e^{-\beta x} (5y^4 - 6y^2c^2 + c^4). \end{aligned} \right\} \quad (14)$$

* In order to calculate these stresses of local character with more accuracy, it would be necessary to increase the number of terms in expression (11), which will entail considerable more calculating work. The calculations made on the compression of the block suggest that the maximum compressive stress obtained above is somewhat exaggerated.

† See Pigeaud, *Comptes Rendus* (Paris, 1915), p. 673.

Fig. 6.



Substituting these expressions in (2), and taking by calculation

$$\int_0^l e^{-\beta x} dx = \frac{1}{\beta},$$

we obtain

$$V = \frac{1}{E} \left\{ \frac{8}{9} \alpha_1^2 \frac{l^3}{c} + \frac{64}{7} \alpha_2^2 \frac{c^7}{\beta} + \frac{128}{11 \cdot 9 \cdot 7 \cdot 5} \alpha_2^2 c^{11} \beta^3 - \frac{64}{105} \sigma \alpha_1 \alpha_2 \cdot c^5 (\beta l - 1) + \frac{256}{9 \cdot 7 \cdot 5} \sigma \alpha_2^2 c^9 \beta + 2(1 + \sigma) \left(\frac{16}{15} \alpha_1^2 c l + \frac{128}{9 \cdot 7 \cdot 5} \alpha_2^2 c^9 \beta - \frac{64}{105} \alpha_1 \alpha_2 c^5 \right) \right\}. \quad (15)$$

The terms involving α_1 , in the expressions (14), correspond to the usual formula for the bending of a narrow rectangular beam. The quantities α_2 and β , corresponding to the "local irregularity" of stress-distribution near the cross-section ($x=0$), we will choose in such a way as to make V a minimum. We thus obtain the equation:

$$\alpha_2 = m \frac{\alpha_1 l}{c^4}, \quad (16)$$

where

$$m = \frac{64}{105} \sigma (\beta c)^2 \cdot \frac{1}{\frac{384}{11 \cdot 9 \cdot 7 \cdot 5} (\beta c)^4 + (1 + 2\sigma) \frac{256}{9 \cdot 7 \cdot 5} (\beta c)^2 - \frac{64}{7}},$$

and

$$\begin{aligned} & \frac{(2 + \sigma)}{2\sigma} \left[\frac{384}{11 \cdot 9 \cdot 7 \cdot 5} (\beta c)^4 + \frac{256}{9 \cdot 7 \cdot 5} (1 + 2\sigma) (\beta c)^2 - \frac{64}{7} \right] \\ &= \frac{l}{2c} \left[-\frac{128}{11 \cdot 9 \cdot 7 \cdot 5} (\beta c)^5 + (1 + 2\sigma) \frac{256}{9 \cdot 7 \cdot 5} (\beta c)^3 + \frac{192}{7} (\beta c) \right]. \quad (17) \end{aligned}$$

From (17) we obtain * values of $\frac{l}{2c}$ corresponding to different values of βc (see table below). With these values of βc we can now calculate, from (16), the values of α_2 . Substituting βc and α_2 in the expression (15) and equalizing it to the work Wf done by the load $2W$, we obtain the deflexion f from the equation

$$f = \frac{Wl^3}{2Ec^3} + \frac{6}{5} \frac{Wl}{2\mu c} - n \frac{Wl}{2\mu c} - q \frac{Wl^3}{2Ec^2}, \quad (18)$$

where

$$\mu = \frac{E}{2(1+\sigma)}; \quad n = \frac{12}{35} \frac{2+\sigma}{1+\sigma} m;$$

$$q = \frac{9}{8} \frac{m}{\beta c} \left\{ \sigma \frac{64}{105} (\beta c)^2 - m \left[\frac{128}{11 \cdot 9 \cdot 7 \cdot 5} (\beta c)^4 + \frac{2(1+2\sigma)}{9 \cdot 7 \cdot 5} 128 (\beta c)^2 + \frac{64}{7} \right] \right\}.$$

Some values of n and q are given in the table below :

βc	=	6	6.5	7	7.07
$\frac{l}{2c}$	=	4.39	8.74	72.0	∞
m	=	0.0363	0.0317	0.0279	
n	=	0.022	0.019	0.017	
q	=	0.019	0.020	0.020	

We see that we may write $n=q=0.02$, in (18), without serious inaccuracy. Then the deflexion may be represented as follows :

$$f = \frac{Wl^3}{2Ec^3} \left(1 + 2.95 \frac{c^2}{l^2} - 0.02 \frac{c}{l} \right). \quad \dots \quad (19)$$

In this manner we can approximately estimate the effect of "local irregularity" of stress-distribution due to the condition that the middle cross-section remains plane

March 7th, 1922.

* In the calculations we have taken $\sigma = \frac{1}{2}$.

CVII. *Diffraction Image of Two Close Luminous Lines of Finite Width.* By B. E. MOURASHKINSKY, *Optical Laboratory of the Central Chamber of Weights and Measures, Petrograd* *.

THE illumination at a point P in a focal plane of a geometrically corrected object-glass with a circular aperture due to an infinite narrow line source is expressed by

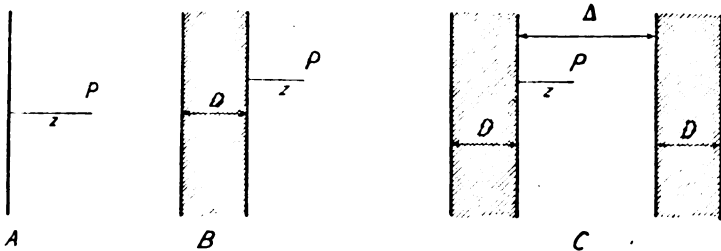
$$I(z) = 3L(z), \quad \dots \dots \dots (1)$$

where

$$z = \frac{2\pi R}{\lambda f} r,$$

r being the linear distance of a point P from the geometrical image of the line source (fig. 1 A).

Fig. 1.



$L(z)$ is the function of Lord Rayleigh :

$$L(z) = \frac{\pi}{2} \frac{H_1(2z)}{(2z)^3}, \quad \dots \dots \dots (2)$$

where $H_1(2z)$ is H. Struve's † function :

$$\begin{aligned} H_1(z) &= \frac{2z^2}{\pi} \int_0^{\frac{\pi}{2}} \sin(z \sin \theta) \cos \theta \, d\theta \\ &= \frac{2}{\pi^2} \left[\frac{z^3}{1^2 \cdot 3} - \frac{z^5}{1^2 \cdot 3^2 \cdot 5} + \frac{z^7}{1^2 \cdot 2^2 \cdot 5^2 \cdot 7} - \dots \right]. \quad \dots (3) \end{aligned}$$

* Communicated by the Author.

† Struve, "Über die Einfluss der Diffraction an Fernrohren auf Lichtscheiben," *Mémoires de l'Académie des Sciences de St. Pétersbourg*, xxx. no. 8 (1882), and *Ann. der Phys.* xvii. p. 1008 (1882).

The function $L(z)$ * by means of (3) may be represented by the series

$$L(z) = \frac{1}{1^2 \cdot 3} - \frac{(2z)^2}{1^2 \cdot 3^2 \cdot 5} + \frac{(2z)^4}{1^2 \cdot 3^2 \cdot 5^2 \cdot 7} - \dots \quad (4)$$

The illumination at a point P given by (1) is expressed in terms of illumination at the geometrical image of a luminous line. We have no complete tables for the distribution of illumination in a diffraction image of a fine line due to a circular aperture except those by André †, calculated by another method not clearly explained in his paper.

As to the limit of resolution of two infinite narrow luminous lines, Lord Rayleigh gives the value 3·14 as the least distance between two lines in order they may be just resolved. The percentage difference between the illumination at its minimum (at the centre of diffraction image) and that at the geometrical images of each line is 4·5. The displacement of maxima (see below) was not considered in Lord Rayleigh's paper.

The illumination at the point P due to a luminous line of finite width may be found in the following manner:—

The expression (1) is to be integrated between the limits z and $z + D$, where

$$D = \frac{2\pi R}{\lambda f} d,$$

d being the linear width of the geometrical image of the line in a focal plane. The z represents now (fig. 1 B) the distance of a point P from the image of the nearer edge of the line. If the point P is outside of the geometrical image of the line, z will be positive; and if P is inside of it, z will be negative. Thus the position of the axis of the line will be noted as

$$z = -\frac{D}{2}.$$

The illumination at a point P is written

$$I(z) = 3C \int_z^{z+D} L(z) dz. \quad \dots \quad (5)$$

The constant C depends on the choice of units. If we express the illumination at P due to a line of finite width in terms of illumination at the same point due to the luminous

* Lord Rayleigh, "Wave Theory," *Encyclopædia Britannica*.

† Ch. André, 'Etude de la Diffraction dans les Instruments d'optique,' 1876.

In Table I. the data noted *a* are the values of illumination calculated by means of (8), those noted *b* the same values referred to the illumination at the axis, and the data noted *c* the positions of maxima or minima (the distances from the edge of the line). The data of this table, as those of the following tables of illumination, are correct to 2-4 units of fourth decimal.

It is seen that even for the width of the luminous line $D=2.0$ two neighbouring maxima and minima differ one from the other only by a very small amount. For values of $D>2.0$ the curves representing the distribution of illumination have no sensible maxima or minima. The illumination at the geometrical image of the edges referred to that at the axis decreases rapidly with increasing D for small values of D and very slowly for large ones, asymptotically approaching the value 0.5 for the semi-infinite plane.

If we have two lines of finite width D at the distance Δ between their inner edges, the illumination at any point P in the focal plane is calculated from the expression :

$$I(z) = \frac{8}{\pi^2} \int_z^\infty L(z) dz - \frac{8}{\pi^2} \int_{z+D}^\infty L(z) dz + \frac{8}{\pi^2} \int_{\Delta-z}^\infty L(z) dz - \frac{8}{\pi^2} \int_{\Delta-z+D}^\infty L(z) dz. \quad (11)$$

The values of the integrals (11) are to be taken directly from Struve's tables. At the axis of the image of each line the illumination will be

$$I\left(-\frac{D}{2}\right) = 1 - 2 \cdot \frac{8}{\pi^2} \int_{\frac{D}{2}}^\infty L(z) dz + \frac{8}{\pi^2} \int_{\Delta+\frac{D}{2}}^\infty L(z) dz - \frac{8}{\pi^2} \int_{\Delta+\frac{3}{2}D}^\infty L(z) dz. \quad (12)$$

At the centre of the diffraction image of two luminous lines the illumination will be

$$I\left(\frac{\Delta}{2}\right) = 2 \left[\frac{8}{\pi^2} \int_{\frac{\Delta}{2}}^\infty L(z) dz - \frac{8}{\pi^2} \int_{\frac{\Delta}{2}+D}^\infty L(z) dz \right]. \quad (13)$$

In the expressions (11), (12), and (13)

$$\Delta = \frac{2\pi R}{\lambda f} b,$$

b being the linear distance (in a focal plane) between the geometrical images of the inner edges (fig. 1 c).

It is evident that two luminous lines of width D are resolved by the same object-glass at different distances Δ between their inner edges for different values of D . The resolution of two such objects depends on the distribution of illumination in the diffraction image or on the contrast between the illumination at its minimum and that at maximum. This contrast will vary with D and Δ .

The angular width of a line and that of the interspace between them are expressed in D and Δ and *vice versa* by means of the following relations :

$$\left. \begin{aligned} D &= \frac{2\pi R}{\lambda} \cdot \tan D'', \\ \Delta &= \frac{2\pi R}{\lambda} \tan \Delta''. \end{aligned} \right\} \dots \dots \dots (14)$$

For given angular values of D'' and Δ'' different object-glasses give different values of D and Δ .

To investigate the diffraction conditions of the resolution of such pairs of close luminous lines of finite width, the values of illumination at the axes of the lines and at the centre of the image were calculated by means of (12) and (13) for different values of D and Δ from 0.2 to 10.0. Thus we can express the illumination at its minimum (at the centre of image) in terms of illumination at the axes of each line for each D and different Δ . Plotting these on millimetre paper (the Δ as abscissæ and the illuminations as ordinates), we have the percentage illumination curves. Extrapolating them graphically, we obtain the values of Δ for which the illumination at its minimum is equal to that at the axes of two lines. The distances thus obtained might be called the critical distances, unless there were not the displacements of maxima for the small values of Δ . The maxima of illumination for small values of Δ do not coincide with the positions of the geometrical images of the axes of two lines, but are displaced symmetrically towards the centre of the image. To find the values of true maxima and values of their displacements with respect to the axes, the illumination was calculated by means of (11) for the whole illumination curve, especially for the points near the axes, and the values of the maxima and their displacements were found graphically. The values of the displacements of the maxima are given in Table II. So as to insert all the data in one table, the distances between two lines are given not in Δ , but in distances between the axes $\Delta + D$. The

TABLE II.

[illegible]

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displacements are expressed in the same units as D or Δ ; thus for $D=0.2$ and $\Delta+D=2.9$ (*i.e.* $\Delta=2.7$) the maxima are displaced from the axes by 0.76 in the same units towards the centre of the diffraction image.

As we see from Table II., the values of displacements of maxima decrease with increasing $\Delta+D$ and generally increase with increasing D for a given $\Delta+D$. As these values are obtained graphically, they are only correct to 3-4 units of the second decimal place, and for this reason the last displacements are not given for less than 0.04 . The distances $\Delta+D$ for which the displacements of maxima are less than 0.04 may be considered as having no displacements. From the same table we see that for the small values of D and $\Delta+D$ the maxima may occur even outside of the geometrical images of lines. For example, for $D=0.4$ and $\Delta+D=3.0$ (*i.e.* $\Delta=2.6$) the displacement of maxima is 0.56 (in the same units); thus they are 0.36 outside of the geometrical images of the inner edges of the lines.

The complete tables of distribution of illumination in diffraction images of two luminous lines for different D and Δ are too long to be given here in full. The values of illumination at the most interesting points of the illumination curves for a number of D are given here as a short abstract of the computed tables. In Table III. M_0 denotes the illumination at the axis of each line, M the maxima of illumination, m the illumination at the central minimum between geometrical images of lines. In the last column are given the percentage ratios of illumination at its minimum to that at the axes or at maxima. We see that values under M_0 have a fluctuating character depending on the fluctuations of the illumination curves of each line taken separately. So that, for example, the values of M_0 for $D=0.2$ have a minimum for $\Delta=3.4$ and a maximum for $\Delta=4.4$; but as is seen from Table I., the luminous line of width $D=0.2$ has its first minimum at 3.5 and first maximum at 4.5 , *i.e.* just on the axis of the other line of width $D=0.2$. Analogously for $D=0.8$ the values of M_0 have a minimum for $\Delta=2.9$ and maximum for $\Delta=3.8$. From Table I. we have that the line of width $D=0.8$ has its first minimum at 3.3 and first maximum at 4.2 , so that $3.3 - \frac{D}{2} = 3.3 - 0.4 = 2.9$ and $4.2 - \frac{D}{2} = 3.8$. For the values of $D=2.0$ and larger we have not these fluctuations of M_0 .

TABLE III.

D = 0.2.					
Δ .	M_0 .	M.	m .	$\frac{m}{M_0} \cdot 100$.	$\frac{m}{M} \cdot 100$.
2.7	0.580	0.605	0.602	103.8	99.5
2.8	0.573	0.588	0.578	100.9	98.3
3.0	0.564	0.569	0.526	93.3	92.4
3.2	0.559	0.560	0.478	85.6	82.4
3.4	0.556		0.432		77.7
3.6	0.558		0.384		68.8
3.8	0.561		0.340		60.6
4.0	0.562		0.300		53.4
4.2	0.563		0.262		46.5
4.4	0.566		0.226		39.9
4.6	0.564		0.194		34.4
4.8	0.562		0.164		29.2
5.0	0.561		0.138		24.6

D = 0.4.					
Δ .	M_0 .	M.	m .	$\frac{m}{M_0} \cdot 100$.	$\frac{m}{M} \cdot 100$.
2.5	1.159	1.209	1.206	104.1	99.8
2.6	1.146	1.174	1.154	100.7	98.3
2.8	1.127	1.134	1.056	93.7	93.1
3.0	1.116	1.118	0.958	85.8	85.7
3.2	1.112		0.862		77.5
3.4	1.114		0.772		69.3
3.6	1.119		0.682		60.9
3.8	1.122		0.602		53.7
4.0	1.125		0.526		46.8
4.2	1.128		0.456		40.4
4.4	1.127		0.390		34.5
4.6	1.123		0.332		29.6
4.8	1.119		0.280		25.0
5.0	1.114		0.234		21.0

D = 0.6.					
Δ .	M_0 .	M.	m .	$\frac{m}{M_0} \cdot 100$.	$\frac{m}{M} \cdot 100$.
2.3	1.736	1.813	1.808	104.2	99.7
2.4	1.715	1.760	1.734	101.1	98.5
2.6	1.686	1.698	1.586	94.1	93.4
2.8	1.671		1.440		86.2
3.0	1.663		1.298		78.1
3.2	1.665		1.162		69.8
3.4	1.671		1.034		61.9
3.6	1.676		0.910		54.3
3.8	1.681		0.796		47.4
4.0	1.683		0.690		41.0
4.2	1.683		0.594		35.3
4.4	1.677		0.506		30.2
4.6	1.671		0.428		25.6
4.8	1.663		0.360		21.6
5.0	1.655		0.300		18.0

Table III. (*continued*). $D = 0.8.$

$\Delta.$	$M_0.$	$M.$	$m.$	$\frac{m}{M_0} \cdot 100.$	$\frac{m}{M} \cdot 100.$
2.1	.2306	.2416	.2414	104.7	99.9
2.2	.2279	.2343	.2316	101.6	98.8
2.4	.2238	.2258	.2118	94.6	93.8
2.6	.2215	.2219	.1926	87.0	86.8
2.8	.2206		.1740		78.9
3.0	.2207		.1560		70.7
3.2	.2212		.1388		62.7
3.4	.2220		.1228		55.3
3.6	.2226		.1074		48.3
3.8	.2228		.0934		41.9
4.0	.2227		.0806		36.2
4.2	.2222		.0690		31.1
4.4	.2213		.0586		26.5
4.6	.2203		.0494		22.4
4.8	.2193		.0416		19.0
5.0	.2182		.0348		15.9

 $D = 1.0.$

$\Delta.$	$M_0.$	$M.$	$m.$	$\frac{m}{M_0} \cdot 100.$	$\frac{m}{M} \cdot 100.$
1.9	.2873	.3019	.3016	105.0	99.9
2.0	.2837	.2924	.2836	102.1	99.0
2.2	.2784	.2813	.2656	95.4	94.4
2.4	.2754	.2761	.2418	87.8	87.6
2.6		.2742	.2188		79.8
2.8		.2740	.1966		71.8
3.0		.2744	.1754		63.9
3.2		.2754	.1552		56.4
3.4		.2760	.1366		49.5
3.6		.2762	.1190		43.1
3.8		.2760	.1030		37.3
4.0		.2755	.0886		32.2
4.2		.2747	.0756		27.5
4.4		.2733	.0642		23.5
4.6		.2719	.0542		19.9
4.8		.2708	.0458		16.9
5.0		.2692	.0386		14.3

Table III. (continued).

D = 2.0.					
Δ .	M_0 .	M.	m .	$\frac{m}{M_0} \cdot 100$.	$\frac{m}{M} \cdot 100$.
1.0	5454	5639	5612	103.3	99.5
1.2	5375	5503	5400	100.5	98.1
1.4	5284	5333	4982	94.3	93.4
1.6	5227	5240	4570	87.4	87.2
1.8		5194	4168		80.2
2.0		5178	3782		73.0
2.2		5171	3412		66.0
2.4		5169	3060		59.2
2.6		5159	2730		52.8
2.8		5166	2424		46.9
3.0		5158	2140		41.5
3.2		5145	1880		36.5
3.4		5131	1646		32.1
3.6		5112	1436		28.1
3.8		5093	1250		24.5
4.0		5075	1090		21.5

D = 3.0.					
Δ .	M_0 .	M.	m .	$\frac{m}{M_0} \cdot 100$.	$\frac{m}{M} \cdot 100$.
0.3	7545	7976	7974	105.7	100.0
0.4	7456	7757	7718	103.5	99.5
0.6	7310	7451	7208	98.6	96.7
0.8	7199	7266	6706	93.2	92.3
1.0	7120	7150	6212	87.2	86.9
1.2	7066	7078	5728	81.1	80.9
1.4	7030	7033	5262	74.9	74.8
1.6		7007	4816		68.7
1.8		6992	4388		62.8
2.0		6980	3986		57.1
2.2		6970	3608		51.8
2.4		6958	3252		46.7
2.6		6943	2922		42.0
2.8		6928	2618		37.8
3.0		6901	2362		34.2
3.2		6894	2090		30.3
3.4		6878	1866		27.1
3.6		6863	1662		24.2
3.8		6851	1482		21.6
4.0		6840	1326		19.4

Plotting the data of the last columns of all the Tables III. for each D on millimetre paper, we obtain the percentage illumination curves. Extrapolating them graphically, we have the distances for which the illumination at central minimum

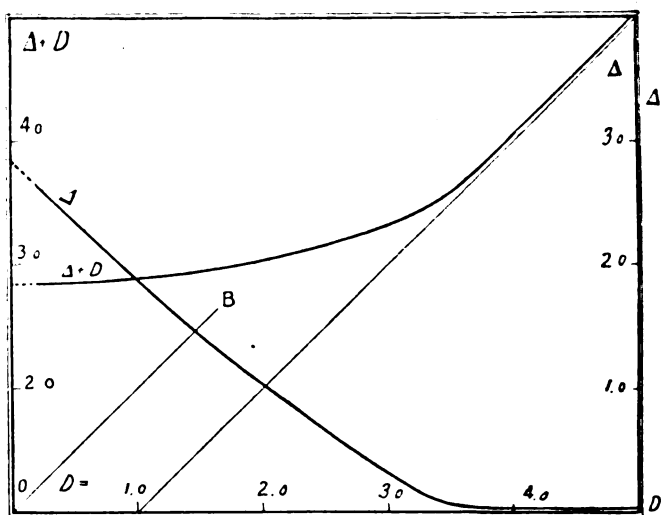
is equal to that at maximum (generally not at the axes), for different values of D from 0.2 to 10.0. These distances are the *critical distances* and are considered as *absolute limits of resolution* of these lines. The critical distances thus obtained, expressed in Δ or in $\Delta + D$, are given in Table IV. and fig. 2.

TABLE IV.

D.	$\Delta_{cr.}$	$\Delta + D_{cr.}$	D.	$\Delta_{cr.}$	$\Delta + D_{cr.}$	D.	$\Delta_{cr.}$	$\Delta + D_{cr.}$
0.2	2.65	2.85	2.2	.90	3.10	4.2	.64	4.24
0.4	2.55	2.85	2.4	.75	3.15	4.4	.64	4.44
0.6	2.26	2.86	2.6	.60	3.20	4.6	.64	4.64
0.8	2.07	2.87	2.8	.45	3.25	4.8	.64	4.84
1.0	1.88	2.88	3.0	.30	3.30	5.0	.64	5.04
1.2	1.70	2.90	3.2	.20	3.40	6.0	<.04	<6.04
1.4	1.52	2.92	3.4	.10	3.50	7.0	<.04	<7.04
1.6	1.36	2.96	3.6	.06	3.66	8.0	<.04	<8.04
1.8	1.20	3.00	3.8	.05	3.85	9.0	<.04	<9.04
2.0	1.05	3.05	4.0	.05	4.05	10.0	<.04	<10.04

Fig. 2.

A.C.



We see that for larger values of D the critical distances are less, so that the broader lines are resolved at less distances between edges. For small values of D the critical distances decrease rapidly; for the large ones they decrease very slowly, approaching asymptotically zero for two semi-infinite luminous planes.

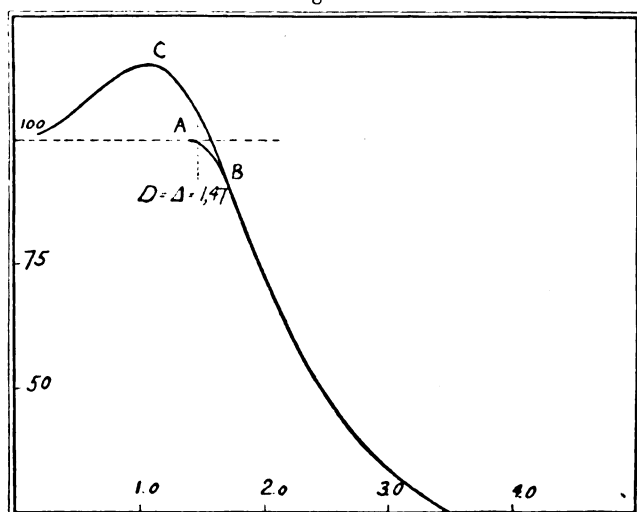
If we have two luminous lines of variable width D with distance Δ between the inner edges, Δ being always equal to

the width of each line, the critical distance for this case may be found graphically by means of the curve Δ_{cr} of fig. 2. The intersection of the line OB ($D=\Delta$) with the curve Δ_{cr} gives the critical distance for $D=\Delta$; it is equal to 1.47, or $D+\Delta=2.94$. (The critical distance for two luminous points of equal brightness is equal to 3.0*.)

TABLE V.

$\Delta=D.$	$\frac{m}{M_0} \cdot 100.$	$\frac{m}{M} \cdot 100.$	$\Delta=D.$	$\frac{m}{M_0} \cdot 100.$
1.6	96.6	98.1		
1.8	85.4	85.5		
2.0	73.0			
2.2	61.7		4.2	16.7
2.4	52.5		4.4	14.9
2.6	44.9		4.6	13.5
2.8	38.8		4.8	12.3
3.0	34.2		5.0	11.4
3.2	29.8		6.0	9.2
3.4	26.4		7.0	8.5
3.6	23.5		8.0	7.8
3.8	20.9		9.0	7.0
4.0	18.7		10.0	6.2

Fig. 3.



As the case $D=\Delta$ may be of some practical interest in treating resolving powers of an object-glass, the values of illumination at the centre of image with reference to that at maximum are given in Table V. and fig. 3.

* B. E. Mourashinsky, "Diffraction Pattern in a case of two very close Point-Light Sources," *Phil. Mag.* xlv, p. 29 (1923).

The intersection of the curve AB with the line 100 (fig. 3) gives once more the critical distance for this case. It is equal, as said, to 1.47 if the displacements of maxima, as it is necessary, are taken into account. For comparison sake, the curve of percentage illumination at the centre of image with reference to that at axes is given in fig. 3 (the curve BC). In this case the distance at which the illumination at the centre is equal to that at the axis is equal to 1.58. For the values $\Delta = D$ greater than 1.84, both the curves coincide.

Extrapolating the curve Δ_{cr} in fig. 2, we obtain the critical distance for $D=0$ (two infinite narrow luminous lines); it is equal to 2.85. Neglecting the displacements of maxima and extrapolating the curve of distances, for which the illumination at the centre is equal to that at the axes, we have that for $D=0$ the corresponding distance is 3.03.

In treating the problem of resolution of two close luminous lines of finite width by an object-glass, it is necessary to know the distribution of illumination along a line perpendicular to geometrical images of the edges of each line. But besides that it is necessary to know the contrast sensibility of the eye. The latter is known only for a case of two adjacent fields for different values of brightness of the fields; but for the diffraction image of two luminous objects, as two luminous lines, the case of adjacent fields cannot be applied. There are, as far as we know, no experimental determinations of contrast sensibility of the eye for a distribution of illumination having a minimum with rapid or slow increase. *A priori*, it might be said that for different values of brightness of the sources the contrast sensibility of the eye will be different.

Assuming the contrast sensibility of the eye to be equal to 5, 10, 15, 20, or 25 per cent., the limit distances Δ between the edges of two lines of different width D could be obtained from the curves representing the last columns of Table IV. They are given in Table VI. and fig. 4.

In testing the quality of an optical instrument, say an object-glass, two different methods may be used. The first is to test all the errors (aberrations) separately; the second to test the instrument in its whole, for example, by the determination of its resolving power. The first method as relating to the linear aberrations or to the aberrations of wave-front does not give a definite answer to the general performance of the instrument, as we do not know till now the accurate (numeric) relations between the aberrations taken as a whole and the resolving power of the instrument.

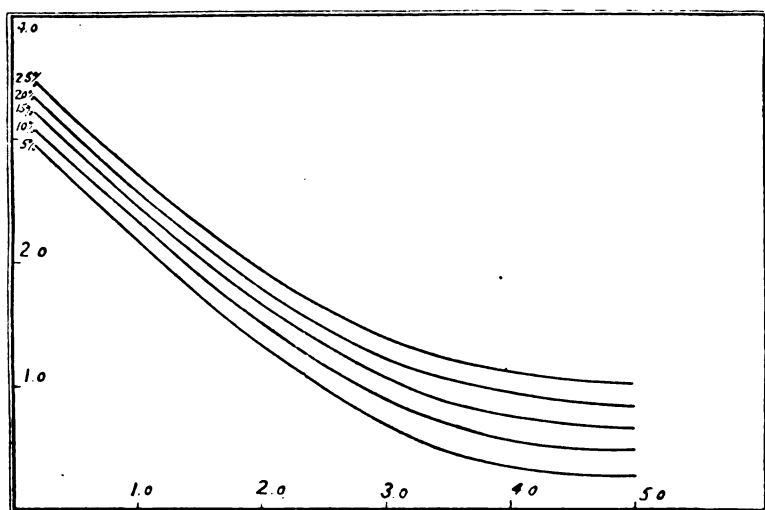
TABLE VI.

D = 0.2.		0.4.	0.6.	0.8.	1.0.	1.2.	1.4.	1.6.	1.8.	2.0.	2.2.	2.4.	2.6.	2.8.	3.0.
5 per cent. ...	2.95	2.75	2.56	2.36	2.18	2.00	1.84	1.67	1.51	1.34	1.20	1.06	.92	.79	.68
10 " ...	3.07	2.89	2.70	2.52	2.34	2.18	1.99	1.82	1.67	1.52	1.37	1.24	1.11	1.00	.90
15 " ...	3.21	3.03	2.82	2.65	2.47	2.30	2.13	1.97	1.82	1.68	1.57	1.40	1.28	1.17	1.06
20 " ...	3.33	3.14	2.95	2.77	2.59	2.42	2.25	2.11	1.94	1.80	1.68	1.54	1.42	1.32	1.22
25 " ...	3.46	3.25	3.08	2.90	2.72	2.56	2.38	2.24	2.08	1.96	1.83	1.70	1.58	1.48	1.39
D = 3.2.		3.4.	3.6.	3.8.	4.0.	4.2.	4.4.	4.6.	4.8.	5.0.	6.0.	7.0.	8.0.	9.0.	10.0.
5 per cent. ...	.59	.50	.41	.38	.34	.32	.30	.29	.28	.27	.26	.24	.22	.21	.21
10 " ...	.80	.72	.67	.60	.56	.53	.51	.49	.48	.47	.44	.42	.40	.39	.39
15 " ...	.97	.90	.85	.80	.76	.73	.70	.68	.67	.65	.62	.60	.58	.58	.58
20 " ...	1.15	1.08	1.02	.98	.94	.91	.89	.86	.84	.83	.80	.79	.77	.76	.76
25 " ...	1.32	1.25	1.19	1.15	1.13	1.10	1.06	1.04	1.02	1.02	.99	.97	.96	.95	.95

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The second method may give a general characteristic of the instrument, but only in the case of our knowledge of theoretical value of resolving power of an *ideal object-glass*, as by the discrepancies (found experimentally) from this theoretical value it is possible to judge about the quality of the instrument. The theoretical values of resolving power of an object-glass based on the distribution of

Fig. 4.



illumination in a diffraction image for several luminous objects (two points, two planes, two lines) were investigated for this purpose. But, as said before, so as to state the *practical limit of resolution of an ideal object-glass* for such objects, it is necessary to know the contrast sensibility of the eye for the distribution of illumination like that in a diffraction image of two luminous objects and for a given brightness of them.

The author is much indebted to Mr. G. Wahrlich for execution of the drawings and for assistance in computations.

CVIII. *The Complexity of the Elements.*—Part I. *Elements of Odd Atomic Number**. By A. S. RUSSELL, M.A., D.Sc., Student and Tutor of Christ Church, Oxford †.

§ 1. Introduction.

IN a previous paper ‡ the writer has shown that there is evidence for the possible existence of four disintegration series, the members of which have atomic weights given respectively by $4n+3$, $4n+2$, $4n+1$, and $4n$, where n is an integer. In that paper reasons are given for supposing that the first of these is the actinium series, the second the uranium series, the third a hypothetical series the end products of which may be bismuth ($a=209$) and thallium ($a=205$), and the fourth the thorium series. The properties of a group of radioactive isotopes were compared with those of a group of isotopes belonging to an inactive element and points of similarity and of difference discussed. The purpose of this paper is to elaborate this comparison in order to see what light the known properties of isotopes of the radio-elements may throw on those of inactive elements. It has been found possible, by boldly applying to the inactive elements what is known to exist for, or is hinted at by the radio-elements, to predict with some degree of confidence the mass-numbers of both even and odd elements over a wide, although not a complete range of atomic numbers. In this work great use has been made of the accepted atomic weights of the elements but, as far as possible, I have tried to develop the results independently of Aston's published experimental values of mass-numbers so that these latter may be made use of as a check on the predictions. In this paper elements of odd atomic number will be chiefly considered.

§ 2. Radioactive and common Isotopes.

The disintegration series as derived in my earlier paper are set out in fig. 1 to show the relation of atomic weights to atomic number and to illustrate the points to be developed.

It may be seen from the figure that if bodies which emit α -particles only are considered (end-products must count as

* A preliminary account of this work appeared in 'Nature,' vol. cxii. p. 588 and p. 619 (1923).

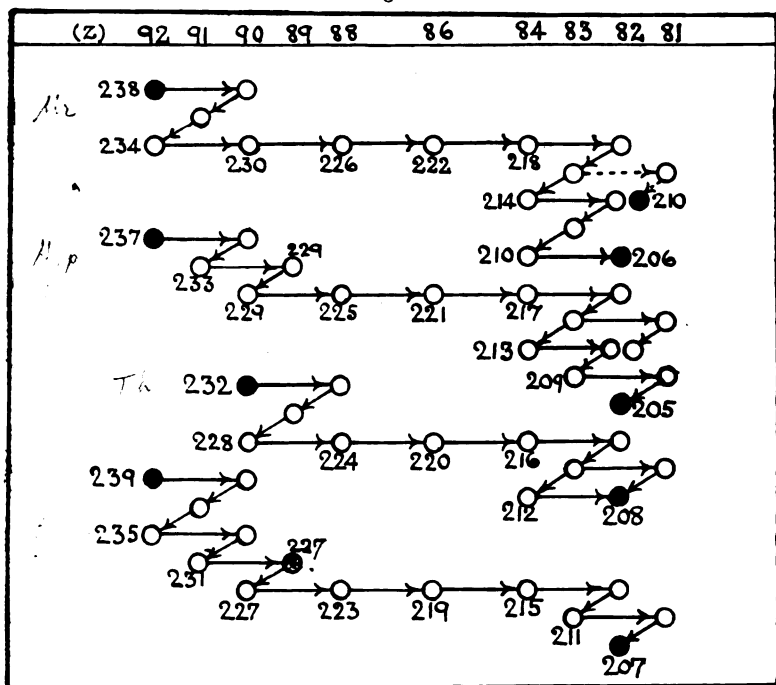
† Communicated by the Author.

‡ A. S. Russell, *Phil. Mag.* xlv. p. 642 (1923).

α -rays, but not bodies which branch principally in the β -direction):—

- (a) The maximum difference in mass-number of any group of isotopes is 8. This holds for the inactive elements investigated by the positive-ray method, the lowest element to show this maximum difference being selenium ($z=34$).

Fig. 1.



- (b) Elements of odd atomic number may have two odd mass-numbers only and these differ by two units. This has been pointed out by Aston* as holding for all elements of odd atomic number so far investigated by him.
- (c) Elements of even atomic number may have both odd and even mass-numbers and, if elements 84 and 92 be excepted, the number of the former is limited to two and their difference is two units. There are no definite exceptions to this among Aston's results. The most complex elements so far investigated by him, numbers 80, 54, 50, and 36, have each two odd isotopes differing by two units of mass-number.

* F. W. Aston, Phil. Mag. xxxix. p 611; xl. p. 628; xlii. p. 140; xlii. p. 436.

The reason for excluding β -rayers in making these comparisons is that these bodies have relatively quick periods compared with their α -ray isotopes, so that if a radio-element was regarded as a common element containing isotopes the β -ray isotopes would be present in negligibly small proportion. This exclusion, however, does not allow of the existence of isobares amongst radioactive isotopes and, in consequence, makes the radio-elements appear less complex than the inactive elements, for these possess, as Aston has shown, isobares. This reasonable objection is removed with respect to even mass-numbers and, at the same time, the comparisons above remain as before, if the second β -rayer of a change involving the expulsion of two successive β -particles alone be excluded. The second β -rayer has invariably a smaller period than the first, the ratio of the periods of the two varying from 3.2×10^{-5} to 0.73.

It may be noted also that in the "repeated" change, that of radium A ($a=218$) to radium Ω' ($a=206$), the periods of each body in the series from radium D ($a=210$) to radium Ω' is much greater than that of its isotope between radium B ($a=214$) to radium D. This is the only certain change of this type in radioactivity, but if it were typical then the element, $z=91$, $a=231$, would have a greater period than $z=91$, $a=233$, and $z=83$, $a=209$, than $z=83$, $a=211$. This is the merest hint that the lighter of the two isotopes of an odd element is the more prevalent in Nature. On examining the values of the atomic weights of the inactive elements and such results as Aston has already obtained experimentally, it is found that this rule appears to hold without exception for the isotopes of inactive elements of odd atomic number. There are indeed elements where the proportion of heavier to lighter isotope is nearly unity but none in which unity is exceeded.

There are two more relations hinted at rather than clearly expressed by the numbers in fig. 1. The first is that the difference $\frac{a_1 + a_2}{2} - 2z$, where a_1 and a_2 are the mass-numbers of an odd element of atomic number z , applies to one element only; the second is that the difference $a - 2z$, where a is the odd mass-number of an even element of atomic number z , applies to one element only. Neither of these holds for the radio-elements as arranged in fig. 1, as Tables I. and II. show. This may be because these relations are false ones; or it may be that not all the elements postulated in fig. 1 actually exist. Nevertheless, the relations will be made use of in what follows as empirical ones, as relations

likely to provide a minimum amount of information concerning the mass-numbers of inactive elements of odd atomic number. Should this information be consistent with experimental results these relations may be applied strictly to the radio-elements.

TABLE I.

$a_1 + a_2 - 2z$	a_1	a_2	z
52	235	237	92
50	231	233	91
48	227	229	90
48	223	225	88
48	219	221	86
46	213	215	84
44	209	211	83
42	205	207	82

TABLE II.

$a - 2z$	a	z
53	237	92
51	235	92
49	229	90
49	225	88
49	221	86
49	217	84
47	227	90
47	223	88
47	219	86
47	215	84
45	213	84
43	207	82
41	205	82

There is one respect at least in which the isotopes postulated in fig. 1 differ from those experimentally discovered by Aston. In all Aston's results* the odd isotopes of even elements are never the lowest in mass-number; according to fig. 1, however, odd isotopes are the lowest in three cases out of six. It would indeed appear that by analogy with Aston's results the hypothetical series is the actinium series and *vice versa*. It will be shown in a later paper, partly from experimental work and partly by the arguments of this paper, that this need not be so and that the contradiction between the two sets of results is more apparent than real.

There is thus a *prima facie* case for considering that radioactive isotopes are not markedly different from those of the inactive elements.

* F. W. Aston, Phil. Mag. xlv. p. 944 (1923).

It is clear from fig. 1 that a succession of α -particles and the succession α, β, α are the characteristic radioactive changes of the two even series, and a succession of α -particles and probably the succession $\alpha, \beta, \alpha, \beta$ of the odd series. If it were imagined that these series continued below the so-called end-products, it is simplest to assume that the former set of changes are characteristic of elements of even atomic number and the latter of elements of odd atomic number. This, however, is not enough. The two odd series in fig. 1 do not pass from elements 89 to 83 through the odd elements 87 and 85, but, like the even series, through 88, 86, and 84. But if these odd series are assumed to continue through inactive elements both or at least one must be imagined as passing through odd elements only, since the even series pass through the even elements, and there are as many odd elements in Nature as even. In other words, if the isotopes of the inactive elements are being or have been produced by the processes of radioactivity it might be that the odd, radioactive series are not wholly characteristic because of the non-existence (supposedly due to instability) of elements 93, 87, and 85.

The main assumption above does not necessarily involve the production of the inactive elements by disintegration, but merely states that the isotopes of inactive elements, however they have been produced in the past, are stable or unstable dispositions according as they would be presumed stable or unstable on radioactive evidence. This is reasonable and not new*. If it leads to a satisfactory agreement between experimental and predicted values of the mass-numbers of the inactive elements, it may reveal a law which may throw light on the stability and composition of the nucleus and the relation of the radio-elements to the inactive elements.

§ 3. Possible Mass-Numbers of Odd Elements.

The odd elements will first be considered. Bismuth ($z=83, a=209$) is taken as datum and the assumption made that odd elements of the form $z=4n+3$ have been genetically connected like the members of a radioactive series, α - and β -like particles only having been expelled. The difference in a corresponding to 4 in z may thus be 8, 12, or

* W. Kossel, *Phys. Zeit.* xx. p. 265 (1919). W. D. Harkins, *Phys. Review*, xv. p. 73 (1920); J. Amer. Chem. Soc. xlii. p. 1956 (1920); *Phil. Mag.* xlii. p. 305 (1921). S. Meyer, *Wien. Ber.* cxxiv. p. 249 (1915). A. van den Broek, *Phys. Zeit.* xvii. p. 260 (1916); xxi. p. 337 (1920).

16 only. The atomic weight of the elements is used as a guide in deciding which of these differences of a is the most probable. The same is done for elements of the form $z=4n+1$, thallium ($z=81, a=203$) being taken as datum. For simplicity I make the limiting assumption that the differences in a are the same for corresponding members of the two series, *i. e.* that both series have disintegrated similarly.

The results of this are tabulated in Table III.

TABLE III.

Range $z=85$ to $z=19$.

z .	a .	δa .	a .	z .
83	(209)		215	85
		12		
79	197		(203)	81
		12		
75	185		191	77
		8		
71	177		183	73
		12		
67	165		171	69
		12		
63	153		159	65
		12		
59	141		147	61
		8		
55	133		139	57
		12		
51	121		127	53
		12		
47	109		115	49
		12		
43	97		103	45
		8		
39	89		95	41
		8		
35	81		87	37
		12		
31	69		75	33
		12		
27	57		63	29
		8		
23	49		55	25
		8		
19	41		47	21

I next assume that each odd element may have like the radioactive elements (§ 2 (b)) two isotopes whose mass-numbers differ by two units. In some cases the second mass-number may be one of two alternatives; in others there is no alternative. (For values of $z=4n+3$ there are alternatives only when the difference between the values of a for $z=4n+5$ and $z=4n+1$ in Table III. is 12.) These possibilities are included in Table IV.

TABLE IV.

Possible mass-numbers of elements of atomic number $4n + 3$ over the range of z 83 to 19.

z .	First isotope.	Possible second isotope.
83	209	207, 211
79	197	195, 199
75	185	187
71	177	175, 179
67	165	163, 167
63	153	151, 155
59	141	143
55	133	131, 135
51	121	119, 123
47	109	107, 111
43	97	99
39	89	91
35	81	79, 83
31	69	67, 71
27	57	59
23	49	51
19	41	39, 43

The same assumption is made in compiling Table V. Here, for values of $z = 4n + 1$, there are alternatives for the second isotope only when the difference between the values of a for $z = 4n + 3$ and $z = 4n - 1$ in Table III, is 12.

TABLE V.

Possible mass-numbers of elements of atomic number $4n + 1$ over the range of z 81 to 21.

z .	First isotope.	Possible second isotope.
81	203	205, 201
77	191	193, 189
73	183	181
69	171	173, 169
65	159	161, 157
61	147	149, 145
57	139	137
53	127	129, 125
49	115	117, 113
45	103	105, 101
41	95	93
37	87	85
33	75	77, 73
29	63	65, 61
25	55	53
21	47	45

It is now possible to decide which of the odd elements are simple and which double and to find out the mass-numbers of their isotopes in the following way :—

- (1) Certain odd mass-numbers not likely to belong to odd elements, *i.e.* not in the second columns of Tables IV. and V., are assigned to certain even elements according to a method described in § 4.
- (2) These and other odd mass-numbers are assigned to certain even and odd elements, which are believed to have each *two* odd isotopes according to a different but analogous plan described in § 5. It is then found that certain elements should be simple and they are assigned the mass-numbers nearest to the accepted values of their atomic weights.
- (3) A principle, namely that the complexity of the elements over a certain range is a periodic function of the atomic number, is then revealed, and this helps to coordinate and check results. This is described in § 6.

§ 4. *Elements of Even Atomic Number containing an Isotope of Odd Mass-Number.*

These elements can be picked out from the others by making the following assumptions :—

- (1) that no odd isobares exist (see § 2) ;
- (2) that the mass-numbers in the second column of both Tables IV. and V. belong to the elements assigned to them there ;
- (3) that the difference $a - 2z$ where a is the odd isotope of an even element z applies to one element only. This difference is the so-called “excess weight” of an element, and is called by Harkins the “Isotopic Number.” This assumption was suggested by radioactive evidence and has been discussed in § 2 above.

The values of z and a corresponding to values of $a - 2z$ from 3 to 43, deduced from these assumptions, are included in Table VI.

It is seen that there are alternative values of z and a for values of $a - 2z$ of 35, 23, and 11 only. It is decided in the next section that the lowest values of a and z are the only possible alternatives for each of these differences, and this is indicated already in two of the three cases by Aston's

experimental values. Values of $a - 2z$ less than 9 appear to have no elements to which they can be allotted. This is probably due to the fact that none of the elements in this region of atomic number is sufficiently complex to have an odd isotope. As none of the four values of a , inconsistent with Aston's experimental work, apparently belongs to any element at all, it is possible that if these mass-numbers existed they would belong to the element to which they are assigned in the table.

TABLE VI.

Even elements with odd isotopes.

$a - 2z$.	z .	a .	Experimental evidence in confirmation.
43	82	207	Radioactivity (Ac Ω).
41	82	205	
39	80	199	Aston *.
37	76	189	
35	76	187	—
	72	179	—
	70	175	—
33	70	173	—
31	66	163	—
29	66	161	—
27	64	155	—
25	60	145	—
23	60	143	—
	56	135	—
	54	131	Aston.
21	54	129	Aston.
19	50	119	Aston.
17	50	117	Aston.
15	48	111	—
13	44	101	—
11	44	99	—
	40	91	—
	36	83	Aston.
9	34	77	—
7	30	67	Aston's results are against all these possibilities.
5	28	61	
	24	53	
3	20	43	

* F. W. Aston, Phil. Mag. xlv, p. 944 (1923).

§ 5. *Elements containing Two Isotopes of Odd Mass-Number.*

These elements are distinguished by making use of the assumption mentioned in § 2 that if z be the atomic weight of any element having two odd mass-numbers a_1 and a_2 , then the difference $\frac{a_1 + a_2}{2} - 2z$ is a number which applies to one element only.

On this assumption and making use of previous tables, Table VII. is compiled.

TABLE VII.

Elements having two isotopes of odd mass-number.

$\frac{a_1 + a_2}{2} - 2z$	a_1	a_2	z
42	205	207	82
40	—	—	—
38	195	197	79
36	181	183	73
34	173	175	70
32	165	167	67
30	161	163	66
28	—	—	—
26	151	153	63
24	137	139	57
22	129	131	54
20	121	123	51
18	117	119	50
16	—	—	—
14	107	109	47
12	93	95	41
12	85	87	37
10	79	81	35
8	69	71	31
6	63	65	29
4	45?	47?	21?
2	{ 39	41	19
	{ 35	37	17

Below atomic number 37 a certain regularity which exists above it disappears. This regularity is that for a difference of $z=16$ there is a difference of $a=44$. Below this atomic number also the rule is sometimes contradicted by the experimental evidence.

It is seen that values of $\frac{a_1 + a_2}{2} - 2z$ equal to 40, 28, 16,

(and possibly also 4) appear to have no corresponding value of z , for the only possibilities in these cases are :

$a_1 + a_2 - 2z$.	a_1 .	a_2 .	z .
40	197	199	79
28	157	159	65
16	113	115	49
4	45	47	21

It is decided later (§ 8) that mass-numbers 113 and 157 are unstable ; 199 has already been assigned to element 80, to which it has been proved by experiment to belong and so cannot belong also to element 79. Nothing can be said at this stage for the difference 4, since it may belong to an element 21 in the irregular part of Table VII. It is concluded, therefore, that the differences 40, 28, and 16 cannot be assigned to any element.

It is of course possible that the assumption that the differences in the first column of Table VII. apply each to one element only is unnecessarily simple. It might be that certain differences apply to two or more elements according to some regular principle, but this does not appear likely unless odd isobares exist, and will not be considered here as the problem to be attacked is sufficiently complex when stated in its simplest terms.

There are two consequences of Table VII. The first is that all elements in the range $z=82$ to $z=37$ not included in the last column are simple, if odd, and do not possess more than one odd isotope, if even. Simple odd elements are therefore atomic numbers 39, 43, 45, 49, 53, 55, 59, 61, 65, 69, 71, 75, 77, and 81. These are tabulated with their mass-numbers below. The second is that two of the three differences in the first column of Table VI., which there may be assigned to one of three elements, are now seen to be assignable only to the element of lowest atomic number in each case. By analogy the third difference in that table is also assigned to the element of lowest atomic number. It is found later (§ 8) that the rejected mass-numbers cannot be assigned to any element. Table VI. should in consequence be amended to read as follows :—

$a-2z$.	z .	a .	Experimental evidence in confirmation.
35	70	175	—
23	54	131	Aston.
11	36	83	Aston.

In Table VIII. is given for reference the mass-numbers of the simple odd elements. They are the "first isotopes" of the tables referred to, except in one case where the second isotope is in agreement with the evidence of atomic weight.

TABLE VIII.

Simple elements of odd atomic number.

<i>z.</i>	<i>a.</i>	Reference to Table.	Experimental evidence in confirmation.
81	203	V.	At.-wt. is against *.
77	193	V.	—
75	185	IV.	—
71	177	IV.	—
69	171	V.	—
65	159	V.	—
61	147 or 149	V.	—
59	141	IV.	—
55	133	IV.	Aston; At.-wt.
53	127	V.	Aston; At.-wt.
49	115	V.	Aston.
45	103	V.	—
43	97 or 99	IV.	—
39	89	IV.	Aston.

* A recent determination by Hönigschmid and Kothé gives the value 204.39 (K. Fajans, 'Radioactivity,' p. 129, 1923).

§ 6. *Complexity a Periodic Function of the Atomic Number.*

In Table IX. the atomic numbers of even elements are tabulated according to their arrangement in Tables VI. (as amended) and VII.

TABLE IX

Atomic numbers of elements with and without isotopes of odd mass-number.

No odd isotopes.				One odd isotope.		Two odd isotopes.	
78	74	72	68	76	80	82	
62	58	56	52	60	64	70	66
46	42	40	38	44	48	36	54 50

Elements 36 and 38 alone do not conform to the grouping by difference of 16. But over the range of $z=40$ to $z=82$

inclusive the complexity of even elements with respect to odd isotopes is a periodic function of the atomic number 16.

The simple odd elements included in Table VIII. may also be grouped in a similar way, thus :

81	77	75	71	69
65	61	59	55	53
49	45	43	39	

The odd elements having two isotopes included in Table VII. may also be similarly grouped :

79	73	67
63	57	51
47	41	

Thus the complexity of odd elements over the range of $z=41$ to $z=81$ appears also to be a periodic function of the atomic number 16. It is found by inspection that the difference in a corresponding to that in z of 16 is usually 44. For heavy elements it may be 48 ; for light ones 40 and even occasionally 36. These differences are all of the form $4n$, and their rôle is readily understandable from work on radioactivity.

To illustrate the periodicity of the complexity of the odd elements the mass-numbers are arranged in 8 groups of atomic numbers having the forms $16n+1$, $16n+3$, $16n+5$, $16n+7$, $16n+9$, $16n+11$, $16n+13$, $16n+15$. These are set forth in Table X. The mass-numbers of the elements in the range which is chiefly being considered ($z=39$ to $z=83$) are derived from the tables to which references are made. The investigation is, however, pushed into the region both of higher and lower elements by making use in the former case of the supposed mass-numbers of the stable radio-elements, and, in the latter, by inserting the known mass-numbers of the lowest element of each series, and linking them with the mass-numbers given in the tables of this paper through the mass-numbers of elements that have not been considered here. In this manner new information is obtained, and in Table X. such information is indicated by absence of reference in the column for references. This will be considered in Table XI. below.

In each column of mass-numbers in the table the differences are of the form $4n$ and are, as has been said above, generally 44 or 40.

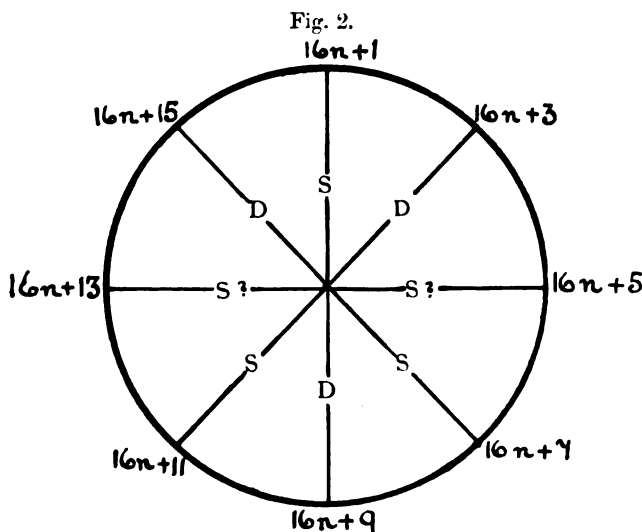
TABLE X.

Atomic Number. <i>z.</i>	Mass- Number.		Reference to Tables.	Atomic Number. <i>z.</i>	Mass- Number.		Reference to Tables.
$(16n+1)$	$a_1.$	$a_2.$		$(16n+9)$	$a_1.$	$a_2.$	
81	203	—	VIII.	89	229	227	
65	159	—	VIII.	73	181	183	VII.
49	115	—	VIII.	57	137	139	VII.
33	75	—		41	93	95	VII.
17	35 or 37			25	—	55	
1	—	1	At.-wt.	9	—	19	At.-wt.
$(16n+3)$				$(16n+11)$			
83	211	209		91	233	—	
67	167	165	VII.	75	185	—	VIII.
51	123	121	VII.	59	141	—	VIII.
35	79	81		43	97 or 99		VIII.
19	39	41		27	—	59	
3	7	5(?) 6)	At.-wt.	11	—	23	At.-wt.
$(16n+5)$				$(16n+13)$			
85	217?	215?		77	—	193	VIII.
69	—	171	VIII.	61	147 or 149		VIII.
53	—	127	VIII.	45	103	—	VIII.
37	85 or 87			29	63	65	
21	45 or 47			13	27	—	At.-wt.
5	9(10)	11	At.-wt.	—	—	—	
$(16n+7)$				$(16n+15)$			
87	221	—		79	195	197	VII.
71	177	—	VIII.	63	151	153	VII.
55	133	—	VIII.	47	107	109	VII.
39	89	—	VIII.	31	71	69	
23	—	51		15	31	—	At.-wt.
7	—	15(14)	At.-wt.	—	—	—	

In the above table the three mass-numbers in brackets are the experimental values; those beside them are those to be expected from the sequence of the mass-numbers of the table to which they belong. It is obvious, however, that elements 3 and 5 cannot have mass-numbers less than 6 and 10 respectively. The discrepancies arise probably because the considerations which led to the prediction of these mass-numbers do not apply to the lightest elements. It is seen that series $16n+1$, $16n+7$, and $16n+11$ are simple. Series $16n+3$ and $16n+15$ are double and $16n+9$ is chiefly double. Series $16n+5$ and $16n+13$ are more irregular than the others but are more simple than double, especially $16n+13$.

A relation between these series is shown in fig. 2. S represents "simple" or "chiefly simple," D "double or "chiefly double." The two irregular series are characterized as S². The line joining $16n+13$ and $16n+5$ divides the figures into opposing halves. About the line joining $16n+1$ and $16n+9$ the figure is symmetrical. A simple relation of this kind

is to be expected if the complexity of the elements be a periodic function of the atomic number.



The new information deducible from the arrangement of Table X. and from fig. 2 is set forth with notes in Table XI.

TABLE XI.

z .	a_1 .	a_2 .	Notes on the Mass-Numbers.	Authority confirming a_1 and a_2 as set out.
83	211	209	$\left\{ \begin{array}{l} a_1 \text{ is probably radioactive, so} \\ \text{that the mass-number of} \\ \text{the element is that of } a_2. \end{array} \right\}$	Radioactivity.
69	171	—	This value appears more probable than 169.	
37	85	87	$\left\{ \begin{array}{l} \text{Nothing can be said as series} \\ 16n+5 \text{ is the most irregular of all.} \end{array} \right\}$	Aston.
35	79	81	Both are certain.	Aston.
33	75	—	a_2 could only be 77 which belongs to $z=34$.	Aston.
31	69	71	Both are certain.	Aston.
29	63	65	The lower is alone certain.	Aston.
27	59	—	Simple element.	Aston.
23	51	—	Simple element.	Aston.
21	45	—	$\left\{ \begin{array}{l} \text{Nothing can be said as series} \\ 16n+5 \text{ is the most irregular of all.} \end{array} \right\}$	Aston.
19	39	41	Both are certain.	Aston.
17	35	37	$\left\{ \begin{array}{l} \text{Only one is certain, and it} \\ \text{cannot be said which is} \\ \text{the more probable.} \end{array} \right\}$	Aston.

§ 7. *Discussion of Results.*

When the mass-numbers which have been calculated by the methods described in this paper and tabulated in the various tables are compared with those actually determined by the positive-ray method or those to be anticipated from reliable determinations of atomic weights, it is seen that discrepancies are most apparent when elements of low atomic number are considered. These are seen in Table II. for the mass-numbers of elements 27 and 23 ; in Table VI. for those of elements 30, 28, 24, and 20 ; in Table VII. for those of elements 37, 29, 21, and 17 ; in Table IX. for elements 38 and 36.

It is clear, then, that if the principle, that the complexity of the elements is a periodic function of atomic number, holds, it holds over a range that does not include the atomic numbers above, *i. e.* it holds over the range of atomic numbers 39 to 83. It will be shown in a subsequent paper that experimental evidence supports, with qualification, the extension of this range to atomic number 92. The obvious cause of failure of the principle to embrace the lower atomic numbers is the relative simplicity of these elements. This is partly borne out by Aston's results. He finds that the largest possible difference in the mass-numbers of isotopes rises from 1 first shown by element 3, to 8 first shown by element 34, being 2 first for element 10, 4 first for element 18, and 6 first for element 32. Since the difference of 8 apparently is not exceeded even by the radioactive elements, it may be taken provisionally as a measure of the possible complexity of an element. There is thus a limit to possible complexity which cannot be attained by elements below number 34. From 34 to 92 there is, in consequence, a chance that some connecting principle may hold.

There are some results in Table X. which appear to be wrong.

(1) Thallium $z=81$ appears to have $a=203$ only. The atomic weight of thallium, which is 204.0 in the International Table, and also fig. 1 suggest very strongly, however, a second isotope at 205. But if this be so, an exception arises both to the simplicity of elements of the series $16n+1$ and also to the existence of isobares of odd mass-number, for there is a probability that element 82 (lead) has an isotope of this mass-number (Table VII.).

(2) It is not likely that gold ($z=79$) has a second isotope at 195, as the table suggests, in any detectable concentration, as the accepted atomic weight is 197.2. It is also exceptional

for the higher of two mass-numbers to be the more abundant. The mass-number 199, on the other hand, is assigned to mercury ($z=80$) (Table VI.) which has received experimental confirmation by Aston, and is consequently ruled out unless odd isobares exist. The difficulty appears best resolved by regarding gold as 197 with a small, probably, negligible amount of 195, i. e. practically a simple element.

(3) Lanthanum ($z=57$) if double is also more abundant in its higher isotope 139 than in its lower 137. The atomic weight in the International Table is 139.0 although several experimental determinations fall below this value. The atomic weight evidence against the simplicity of this element is consequently conflicting.

It is a possible inference from (2) and (3) that some elements which appear to be double in form may really be single. Such have atomic weights which approximate to the higher of their possible mass-numbers. In all such cases the lower cannot apparently be assigned to another element and is, in consequence, a missing mass-number.

It will be shown in a later paper which deals with the mass-numbers of even elements that periodicity is shown there more strikingly than with odd elements. Periodicity is, however, least in agreement with the apparent facts in the series of elements whose mass-numbers are of the form $16n+15$ and $16n+13$. These series correspond, by analogy, with the groups of the Periodic System (such as groups VI. A and I. B) in which the chemical resemblances of members are by no means marked. It is impossible to predict with any confidence the complexity of elements of this series, and the uncertainty is likelier to obtain for the lighter than for the heavier members.

It is noticeable that several elements of the double series $16n+3$ and $16n+15$ have isotopes in nearly equal proportion as judged from evidence of atomic weight: elements 35 and 51 in the former series, and 31, 47, 63 (not 79, however, but perhaps 81) in the latter. In the third double series $16n+9$, however, the mean atomic mass of the elements approximates to that of one of its isotopes.

§ 8. Missing Odd Mass-Numbers.

There appears to be three definite groups of missing odd mass-numbers, and these may be derived from the numbers given in Table X. Each of the series $16n+1$, $16n+7$, and $16n+11$ is simple. The inclusion of certain mass-numbers

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in each would make them double. As none of these mass-numbers are assignable to elements of even number (Table VI.) they are presumably missing. The numbers so derived are included in Table XII. and fall into three complete groups. The numbers derived from the incomplete, simple series $16n+5$ and $16n+13$ are also given.

TABLE XII.

Groups of missing odd mass-numbers.

Series from which numbers are derived (Table X.).	Derived missing Mass-Numbers.
$16n+1$	201, 157, 113, 73, 33
$16n+7$	223, 179, 135, 91, 49, 13 53, 17
$16n+11$	231, 187, 149, 99, 57, 21 61, 25
$16n+5$	169, 125
$16n+13$	191, 149 or 147, 105, 29

Of these mass-numbers two only, 25 and 29, have been proved to exist. They fall, however, outside the range that is chiefly being considered here, and, moreover, they do not belong to odd elements but to even ones. The following is the list of missing odd mass-numbers compiled from Aston's work: 201, 73, 67, 61, 57, 53, 49, 47, 43, 33, 21, 17, 15, 13, 5, and 3. All of these except 67, 47, 43, 15, 5, and 3 are included in the table above. 67 and 43 are not derived from, but accounted for, by Table VI. These would be the isotopes of elements 30 and 20 respectively if the latter were sufficiently complex to include odd isotopes. These, unlike the others, are not members of a series of missing mass-numbers. Some explanation involving the simplicity of the very lightest elements might account for the non-existence of 3, 5, and 15. (Analogies would make 15 not 14 the single mass-number of nitrogen.) There remains of Aston's list mass-number 47. Table VII. leaves the question of its existence open; for, by analogy with the mass-numbers of higher elements, scandium ($z=21$) should be single, but this element occurs at a part of the table which does not conform to the simplicity of the greater part. Table X. also is indecisive although the balance of probability is in favour of the existence of 47. There are, however, three further

considerations. The first is that the occurrence of two consecutive, missing, odd, mass-numbers is rare; the second that the existence of a mass-number, of the form $4n+3$, one unit less than that of a simple element seems to be the rule for all mass-numbers above 47. On the other hand, if scandium be double it is one of three consecutive double odd elements, and this appears to be exceptional. On the whole the evidence from analogy is in favour of the existence of 47. Aston's experimental work is not decisively against this view.

A second paper will deal with the isotopes of elements of even atomic number.

§ 9. Summary.

(1) By analogies with and deductions from the properties of the radioactive elements, it is concluded that over a range of atomic number 39 to 83 the complexity of elements appears to be a periodic function of the atomic number 16. The corresponding mass-number is usually 44 or 40.

(2) Elements of odd atomic number are principally considered. It is deduced that the following should be simple; atomic numbers 1, 7, 11, 17, 23, 27, 33, 39, 43, 45, 49, 53, 55, 59, 61, 65, 69, 71, 75, 77, 81, 87, 91. Probably also 57, 79, and 83.

(3) The following should consist of two isotopes: atomic numbers 3, 19, 31, 35, 41, 47, 51, 63, 67, 73, and 89. Numbers 57, 79, and 83 are double in form.

(4) It is not possible to pronounce definitely on the complexity of elements 5, 9, 13, 15, 21, 25, 29, 37, and 85 from these considerations alone.

(5) The elements mentioned in (2) and (3) with their atomic weights, mass-numbers, etc., are given for reference in Table XIII. A blank space denotes there is no information available, a dash that there is no mass-number. The reason for the brackets around a few of the numbers has been explained in § 7.

(6) The following mass-numbers belong to even elements: 77 to 34, 83 to 36, 101 to 44, 111 to 48, 117 and 119 to 50, 129 and 131 to 54, 145 to 60, 155 to 64, 161 and 163 to 66, 173 and 175 to 70, 189 to 76, 199 to 80, 205 and 207 to 82.

TABLE XIII.

Element.	<i>z</i> .	Atomic Weight.	Expected Mass-Numbers.		Experimental Mass-Numbers.	
Pa	91		233	—		
Ac	89		227	229		
	87		221	—		
Bi	83	209.0	209	(211)	209	
Tl	81	204.0	203	—	203?	205?
Au	79	197.2	197	(195)		
Ir	77	193.0	193	—		
	75		185	—		
Ta	73	181.5	181	183		
Lu	71	175	177	—		
Tm	69	168.5	171	—		
Ho	67	163.5	165	167		
Tb	65	159.2	159	—		
Eu	63	152.0	151	153		
	61		147 or 149	—		
Pr	59	140.9	141	—	141	
La	57	139.0	139	(137)	139	
Cs	55	132.81	133	—	133	—
I	53	126.92	127	—	127	—
Sb	51	121.8	121	123	121	123
In	49	114.8	115	—	115	—
Ag	47	107.88	107	109	107	109
Rh	45	102.9	103	—		
	43		97	—		
Nb	41	93.1	93	95		
Y	39	89.33	89	—	89	—
Br	35	79.92	79	81	79	81
As	33	74.96	75	—	75	—
Ga	31	70.1	69	71	69	71
Co	27	58.97	59	—	59	—
V	23	51	51	—	51	—
K	19	39.1	39	41	39	41
Cl	17	35.45	35	—	35	37
Na	11	23.00	23	—	23	—
N	7	14.01	15	—	14	—
Li	3	6.94	5	7	6	7
H	1	1.008	1	—	1	—

(7) The following mass-numbers appear to be missing on analysis: 13, 17, 21, 25, 29, 33, 49, 53, 57, 61, 73, 91, 99, 105, 113, 125, 135, 143, 149 or 147, 157, 169, 179, 187, 191, 201, 223, 231. Probably also 137, 195 and 211.

Dr. Lee's Laboratory,
Christ Church, Oxford.
February 1924.

CIX. *Elastic Impact of Pianoforte Hammer.*
By S. BHARGAVA, M.Sc., and R. N. GHOSH, M.Sc.*

[Plate VIII.]

I.

HELMHOLTZ built up his classical theory of the vibration of pianoforte strings on the assumption that the law of pressure was given by $F \sin pt$ †. He regarded the hammer as elastic, and the duration of impact as small compared with the period of vibration of the string. Later on, Kaufmann ‡ showed that the duration of impact was comparable to the period of vibration of the string, and he based his theory on the assumption that the hammer was hard. Professor Raman and Mr. Banerji § conjointly and Mr. Das || separately have recently extended the theory of the hard hammer, and they have given a method for calculating the duration of impact in the general case when the striking-point lies anywhere in the string. The present paper attempts to develop the theory of impact of the elastic hammer when the duration of impact is comparable to the period of vibration of the string. The theory has been put to test by experiments with hammers and strings actually used in the piano.

II.

Ignoring for the present the shape of the hammer, and its effect on the duration of impact in accordance with the theory of Hertz ¶, we simplify the problem by considering that the hammer is made up of a hard mass backed by a weightless spring, which together impinge upon the string. The shape of the hammer actually used has been chosen in order to increase the effective area of contact, which has the effect of increasing the convergency of partials. With these assumptions we shall now proceed to develop the

* Communicated by the Authors. Read before the Indian Science Congress, January 1923.

† 'Sensation of Tone' (Ellis translation), p. 380.

‡ *Ann. der Physik*, liv. p. 675 (1895).

§ *Proc. Roy. Soc.* xcvii. p. 99.

|| *Proc. Ind. Assoc.* vii. p. 13.

¶ Love's 'Theory of Elasticity,' Art. 139 (1906 ed.).

theory in a few cases. The symbols used in the paper are :

- M = Mass of hammer.
 ρ = Mass of string per cm.
 y = Displacement of the string.
 y_0 = Displacement of the centre of mass of the hammer.
 ξ = Compression of the spring.
 μ = Strength of the spring.
 l = Length of the string.
 T = Tension of the string.
 C = Velocity of transverse wave in the string.
 α = Distance of the striking-point from the nearer extremity.
 t = The time.

Case I.

Length of the string finite.

Let us consider a theoretical case in which the mass of the whole string is supposed to be collected at the point of impact which divides the string into two portions, α and $l-\alpha$. The equation of motion of the hammer is given by

$$\frac{M d^2 y_0}{dt^2} = -p, \quad \dots \dots \dots (1)$$

where p represents the pressure between the hammer and the mass ρl .

$$p = \mu \xi, \quad y_0 = y + \xi. \quad \dots \dots \dots (2)$$

The equation of motion of the mass ρl is

$$\rho l \frac{d^2 y}{dt^2} = p - \frac{T y l}{\alpha(l-\alpha)}. \quad \dots \dots \dots (3)$$

From (1), (2), and (3) we obtain

$$\left. \begin{aligned} \frac{d^4 \xi}{dt^4} + \frac{T}{\alpha(l-\alpha)\rho} \cdot \frac{d^2 \xi}{dt^2} + (\mu K_1 + \mu T/M\rho\alpha(l-\alpha))\xi &= 0, \\ K_1 &= \frac{1}{l\rho} + \frac{1}{M}. \end{aligned} \right\} \quad \dots \dots \dots (4)$$

Assuming $\xi = l^t$, we get

$$s^2 = -(\beta \pm \sqrt{\beta^2 - \gamma}),$$

giving four values of s .

$$2p = \mu K_1 + \frac{T}{\rho \alpha (l - \alpha)},$$

$$\gamma = \frac{T\mu}{M\rho \alpha (l - \alpha)}.$$

Two cases of interest immediately present themselves :—

- (1) When $\mu = \infty$: *i. e.* the hammer is hard, s comes out infinite, or the duration of impact is very small.
- (2) When $\mu = 0$, $s = \pm i T / \rho \alpha (l - \alpha)$: *i. e.* the duration of impact is the same as the period of vibration of the mass ρl .

Case II.

Length of the string finite.

The duration of impact is supposed to be small compared with the period of vibration of the string, which is therefore not appreciably displaced from its equilibrium position (Helmholtz).

$$y_0 = \xi.$$

Eliminating y_0 from (1) and (2) with the help of the above relation, we obtain

$$\frac{M}{\mu} \frac{d^2 p}{dt^2} = -p. \quad \dots \dots \dots (5)$$

$$\therefore p = v_0 (\mu M)^{\frac{1}{2}} \sin \{ \mu / M \}^{\frac{1}{2}} t,$$

where v_0 represents the velocity with which the hammer impinges upon the string. The law of pressure is the same as supposed by Helmholtz. The duration of impact is given by $\pi (M/\mu)^{\frac{1}{2}}$; it depends upon the mass of the hammer and the strength of the spring, but it is independent of the striking distance and the velocity of impact.

Case III.

Length of the string infinite, and it is displaced during impact.

Now

$$p = \mu \xi = 2T \frac{dy}{dx} = \frac{2T}{C} \frac{dy}{dt} \text{ approx. } \dots \dots (6)$$

Eliminating y between (1) and (6), we obtain

$$\frac{M}{\mu} \frac{d^2 p}{dt^2} + \frac{MC}{2T} \frac{dp}{dt} + p = 0, \quad \dots \quad (7)$$

$$p = \frac{v_0 \mu e^{-\frac{1}{4} \frac{MC}{T} t}}{\left\{ \frac{\mu}{M} - \frac{1}{4} \left(\frac{MC}{2T} \right)^2 \right\}^{\frac{1}{2}}} \sin \left\{ \left\{ \frac{\mu}{M} - \frac{1}{4} \left(\frac{MC}{2T} \right)^2 \right\}^{\frac{1}{2}} t \right\} \quad \dots \quad (8)$$

if $\frac{16T\rho}{\mu} > M$, i. e. if the hammer is elastic.

The duration of impact in this case is given by

$$\pi \left\{ \frac{\mu}{M} - \frac{1}{4} \left(\frac{MC}{2T} \right)^2 \right\}^{-\frac{1}{2}}.$$

We observe that the duration of impact for an elastic hammer is finite for infinite length of the string. It is independent of the velocity of the impact, depending mainly upon the mass and elasticity of the hammer. As μ increases, the duration of impact increases, and when μ is large, equation (7) degenerates into

$$\frac{MC}{2T} \frac{dp}{dt} + p = 0, \quad \dots \quad (9)$$

$$p = Ae^{-\frac{2T}{MC} t}, \quad \dots \quad (10)$$

A being a constant to be determined from the initial conditions. Thus we see from (10) that when μ is infinite, the duration of impact is also infinite for a very long string, in agreement with Kaufmann.

Case IV.

Length of the string finite; it is displaced during impact, and α , the striking distance, is small.

Further, we suppose that the portion of the string between the point struck and the nearer end follows the motion of the hammer. This means that the wave takes little time to reach and get reflected from the nearer extremity. The other wave travels onward towards the longer side and reaches the end on the longer side, when the impact is supposed to be over. The former assumption no doubt overestimates the kinetic energy, but the actual facts cannot be far from this. p is then given approximately by

$$p = \mu \xi = T \left\{ \frac{y}{\alpha} + \frac{1}{C} \frac{dy}{dt} \right\}. \quad \dots \quad (11)$$

Eliminating p from (1) and (11), we obtain to a first approximation

$$M_1 \left(1 + \frac{T}{\mu \alpha} \right) \frac{d^2 y}{dt^2} + \frac{T}{C} \frac{dy}{dt} + \frac{Ty}{\alpha} = 0, \quad \dots \quad (12)$$

where

$$M_1 = M + \rho \alpha / 3.$$

$$\therefore y = A e^{-\frac{K}{2} t} \sin q t, \quad \dots \quad (13)$$

$$\left. \begin{aligned} q^2 &= \frac{T}{\alpha M_1} \left(\frac{\mu \alpha}{T + \mu \alpha} \right) - \frac{1}{4} K^2, \\ K &= \frac{T}{M_1 C} \left(\frac{\mu \alpha}{\mu \alpha + T} \right). \end{aligned} \right\} \quad \dots \quad (14)$$

If v_0 is the initial velocity of the hammer at the beginning of impact, A is found to be given by

$$A = \frac{v_0}{q} \left\{ 1 + \frac{T}{\mu} \left(\frac{1}{\alpha} - \frac{K}{2C} \right) \right\}^{-1} \quad \dots \quad (15)$$

From (13) and (15) we find in the case of hard hammer, i. e. $\mu = \text{infinite}$,

$$\left. \begin{aligned} q_1^2 &= \frac{T}{\alpha M_1} - \frac{1}{4} \left(\frac{T}{M_1 C} \right)^2, \\ A_1 &= \frac{v_0}{q_1}. \end{aligned} \right\} \quad \dots \quad (16)$$

The duration of impact in the case of an elastic hammer is given by π/q (approximately); it depends upon the mass of the hammer, its elasticity, and the striking distance α .

From a comparison with q_1 in (16), we observe that the effect of elasticity is to prolong the duration of impact. When the hammer is very soft, μ is very small. The duration of impact becomes infinite, as is also evident on general grounds. The duration of impact increases as α increases. It is, as before, independent of the initial velocity of impinge of the hammer. By comparing (14) and (15), we find that the duration of impact of an elastic hammer when the string is appreciably displaced from its equilibrium position during impact, is greater than that when there is no appreciable displacement of the string.

The amplitude of motion produced in the string is proportional to the initial velocity of impinge, and increases with α and the duration of impact. When μ is very small, the amplitude of motion is also very small; but when μ is

infinite it is finite, as shown by (16). Further, we observe that the amplitude in the case of an elastic hammer is greater than that due to a hard hammer.

III. Experiments.

The hammers used in the piano in the upper octaves are harder and lighter than those used in the middle ranges. The distance of the striking-point is almost the same for all strings; it varies within one-ninth to one-seventh of the length of the string in different types of piano. Hence, in order to test the above formulæ, a sonometer was fixed almost vertically and the hammer was placed near the lower extremity of the sonometer, so that the distance of the point struck from the lower bridge was small. By an arrangement of a lever the hammer was made to strike in a vertical plane—that is, parallel to the plane containing the hammer and the string. The lever arrangement was the same as is used in the piano. The wires and hammers used in the experiments were borrowed from a local piano-tuner, and those were selected which are used in the middle range where the hammer is elastic and heavy. The point of impact was photographed by a sliding plate which recorded the approach and retreat of the hammer. (Care was taken that the hammer did not strike the string a second time, by an arrangement of a catch.) The time was simultaneously obtained from the trace of a style attached to a tuning-fork. In Pl. VIII. figs. 1, 2, 3, 4, and 5 show in ascending order the distance of the point struck. The approach and retreat of the hammer are shown by the parabolic shadow, and the vibration of the point struck and the record of the style are also seen. It is evident from these figures that the duration of impact and the amplitude of the resulting motion increase with increasing distance of the striking-point. These facts are in agreement with those deduced from (14) and (15). Formula (14) can be written in the form:

$$\frac{\phi}{\theta} = \pi / \left[\frac{M_0}{M_1} \left\{ \frac{4l}{\alpha \left(1 + \frac{T}{\mu \alpha} \right)} - \frac{M_0}{M_1} \frac{1}{\left(1 + \frac{T}{\mu \alpha} \right)^2} \right\} \right]^{\frac{1}{2}}.$$

ϕ = Duration of impact.

θ = Period of vibration of the string.

Table I. gives a record of the values at different distances α found experimentally and calculated from (14).

TABLE I.

 $\rho = .0589$ gram per cm. $M_0 = 5.61$ grams. $M = 7.3$ grams (mass of head plus one-third mass of stem). $\theta = \frac{1}{100}$ second.

Length of the string 95.4 cm.

 $T/\mu = 2.64$.

No.	α .	ϕ/θ obs.	ϕ/θ calc. (14).	ϕ/θ Kaufmann.
	cm.			
1 ...	8.2	.607	.604	.52
2 ...	9.8	.64	.65	.60
3 ...	11.5	.704	.706	.63
4 ...	14.3	.80	.79	.75
5 ...	17.7	1.0	.87	.84
6 ...	18.1	1.06	.90	.86

From the table it is clear that the values observed and those calculated from (14) agree fairly, while Kaufmann's formula gives more divergent values than experimental errors justify. Further, it is also confirmed that the duration of impact does not depend upon the velocity of impact, to which no fixed value was imposed during experimentation.

Hence it is concluded that to determine the law of pressure between the hammer and the string, its elasticity must be taken into consideration. In the higher scale of the piano, where the hammer is hard and light, Kaufmann's theory of inelastic impact may hold good. It is also found that the calculated values of ϕ/θ differ from those found experimentally with increasing striking distance. They are less than those observed. This regular decrease in the calculated values points out that our assumption, namely that the portion of the string between the striking-point and the nearer extremity follows the motion of the hammer, does not hold true when α is large, appreciable time being taken by the wave to reach the nearer end and return.

Conclusion.

Since in practice the striking distance is about one-ninth the length of the string, it is thought that the above theory

of the elastic hammer will be of practical value. It is more general than Kaufmann's, and includes his as a special case. The authors hope to calculate the intensity of partials on the basis of the law of pressure given by them, and compare it with experiments and verify formula (15) with different values of r_0 on a future occasion.

Physics Laboratory, Allahabad University,
Allahabad, India,
December 14th, 1922.

CX. The Relation between Uranium and Radium.—
Part VIII. *The Period of Ionium and the Ionium-Thorium Ratio in Colorado Carnotite and Joachimsthal Pitchblende.* By FREDERICK SODDY, M.A., F.R.S., and Miss ADA F. R. HITCHINS, B.Sc.*

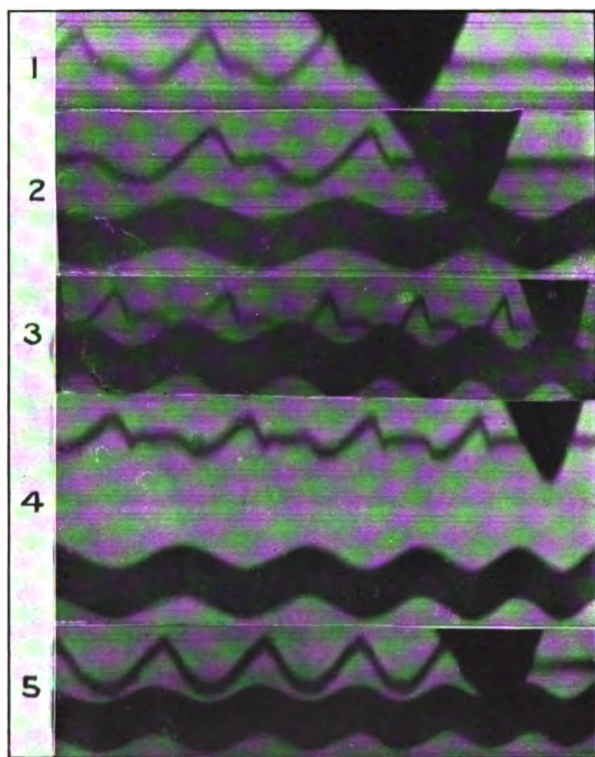
IN the course of a study of the ionium-thorium ratio in minerals, occasion has been taken to redetermine the period of ionium from the rate of growth of radium in the various uranium preparations purified from 18 to 15 years ago, and the new results may first be recorded. It may be recalled that, as the result of the last examination in 1919 (Phil. Mag. [6] xxxviii. p. 483 (1919)), it was found that the rate of growth of radium was proceeding regularly in accordance with the square of the time, with the period of 237,500,000 years as the product of the periods of average life of ionium and radium, which led to the adoption of the period of 100,000 years for that of ionium. The new results are set forth in the same tabular form as in the paper cited. The value of the average life of radium is retained at 2375 years for the sake of uniformity, and the average life of ionium, $1/\lambda_2$, is calculated from the formula

$$1/\lambda_2 = \frac{1}{2}(U/Ra)(3.4 \times 10^{-7}/2375)T^2,$$

where Ra grams of radium are produced from U grams of uranium in T years.

Two sets of determinations have been made, in August and December 1923, of the amount of radium in the four uranium preparations. The electroscope was first calibrated with a number of radium standards, made from a radium barium chloride of known small radium content, one of which was new and the others those previously employed.

* Communicated by the Authors.



Calibration of the electroscope.

Standard g. BaCl ₂ .	Ra ($\times 10^{-12}$ g.).	Divisions per minute.	Constant 10 ⁻¹² g. of radium giving 1 d.p.m.
0.0454	29.6	1.86	15.91
0.2140 (new)	139.5	8.78	15.89
0.2625	171.1	10.91	15.68
0.3981	259.6	16.47	15.76
0.5683	370.5	24.16	15.34
0.7869	512.9	33.02	15.53
Mean			15.69

Before the measurements were repeated in December the electroscope was again calibrated :

0.2704	176.3	11.21	15.73
0.5683	370.5	23.91	15.50
0.7869	512.9	33.36	15.37

Since no significant change had occurred the constant 15.69 was used throughout.

The results are given in the following table:—

Number of Preparation.	Grams Uranium.	Time (years).	(Time) ² .	Radium ($\times 10^{-12}$ g.).	Initial Radium.	Growth of Radium.	Growth of Radium $\div$ (Time) ² .	Ditto. Mean Value.	Period of Ionium (years).
I.	255	17.81	317.2	71.7	16	55.7	0.176	0.175	104,300
		18.15	329.4	73.3		57.3	0.174		
II.	278	17.00	289.0	72.0	18	54.0	0.187	0.189	105,300
		17.34	300.7	75.5		57.5	0.191		
III.	408	16.68	278.2	75.5	4	71.5	0.257	0.2585	113,000
		17.02	289.7	79.4		75.4	0.260		
IV.	3000	14.21	201.9	434.5	40	394.5	1.954	1.958	109,700
		14.54	211.4	454.7		414.7	1.962		
Simple Mean									108,000

For the first time since the start, the older preparations I. and II., in which the initial radium exceeded one part

in 10^{14} of uranium, are sufficiently far advanced to give quantitative evidence, and this is in agreement with that given by the two later preparations. The new mean result is 8 per cent. higher than that arrived at in 1919, and this is somewhat outside the probable degree of accuracy (5 per cent.) then estimated. This would of course be explained by the presence of initial ionium, but in view of the isotopism of uranium X and the known behaviour of the latter under the methods of purification employed, it is practically impossible to believe that sufficient ionium to account for the result was initially present. It seems more natural to ascribe it to the errors of measurement being for some reason larger than was supposed and to round off the value to be adopted for the average life of ionium to

$$\underline{1.1 \times 10^5 \text{ years.}}$$

Determination of the Ionium-Thorium ratio in Minerals.

Provided sufficient can be obtained to weigh, since ionium and thorium are isotopes, the ionium-thorium ratio in a mineral may be obtained, when the period of ionium is known, by separating and purifying the ionium-thorium mixture, with precautions against the adventitious introduction of thorium, and determining the rate of growth of radium in a preparation containing a known weight. Ordinarily, a small uncertainty is introduced, especially in intensely active preparations, by the time of accumulation of the emanation between measurements, during which time the radium itself is changing in quantity,—in an active preparation perceptibly. For a weak preparation in which the emanation may be allowed to attain “transient” equilibrium, the correction is exactly and readily made by subtracting from the total time of accumulation of the radium the period of average life of the emanation. But the correction may be made exactly and readily for any period of accumulation.

The first differential equation of the disintegration series involved, in which I_0 and R_a refer to (atomic) quantities of ionium and radium, λ_2 and λ_3 being their radioactive constants,

$$d(R_a)/dt = \lambda_2 I_0 - \lambda_3 R_a$$

gives, since the second term is negligible relatively to the first,

$$R_a - R_{a_0} = \lambda_2 I_0 t,$$

where R_{a_0} is the initial quantity of radium present and t is the time.

The second differential equation of the series

$$d(\text{Rn})/dt = \lambda_3 \text{Ra} - \lambda_4 \text{Rn},$$

where λ_4 is the constant of radon (radium emanation), gives, by substituting the above value for Ra,

$$\text{Rn} = (\lambda_2 \lambda_3 / \lambda_4) \text{Io} (t - 1/\lambda_4) + \lambda_3 \text{Ra}_0 + C e^{-\lambda_4 t},$$

where C is the integration constant.

Solving for the conditions that $\text{Rn} = 0$, when $t = t_0$, that is, that the time from purification to the time of sealing up the preparation is t_0 , and that the time of accumulation of radon is τ , the total time from purification to measurement being $t_0 + \tau$, gives

$$\lambda_4 \text{Rn} / \lambda_3 (1 - e^{-\lambda_4 \tau}) = \lambda_2 \text{Io} \{t_0 - 1/\lambda_4 + \tau / (1 - e^{-\lambda_4 \tau})\} + \text{Ra}_0.$$

The quantity on the left-hand side of the equation is the quantity of radium measured in the usual way in the emanation method of estimation, being the emanation corrected to equilibrium accumulation and expressed as the quantity of radium with which the corrected quantity of emanation is in equilibrium. [For if a quantity of radium Ra produces a quantity of radon Rn in time of accumulation τ , and Rn_e is the equilibrium quantity,

$$\text{Rn} = \text{Rn}_e (1 - e^{-\lambda_4 \tau}) \quad \text{and} \quad \lambda_4 \text{Rn}_e = \lambda_3 \text{Ra}.$$

Hence $\text{Ra} = \lambda_4 \text{Rn} / \lambda_3 (1 - e^{-\lambda_4 \tau}).$]

Substituting and converting atomic weights to weights gives

$$\text{Ra} - \text{Ra}_0 = \lambda_2 \text{Io} \{t_0 - 1/\lambda_4 + \tau / (1 - e^{-\lambda_4 \tau})\} (226/230). \quad (1)$$

We may designate the expression within {} "the effective time" θ , where

$$\theta = t_0 - 1/\lambda_4 + \tau / (1 - e^{-\lambda_4 \tau}). \quad (2)$$

Putting in the values $1.1 \times 10^5 \times 365$ for $1/\lambda_2$ (days), and 5.555 for $1/\lambda_4$ (days), gives

$$\text{Ra} - \text{Ra}_0 = 2.45 \times 10^{-8} \text{Io} \theta, \quad (3)$$

and $\text{Io} = 4.08 \times 10^7 (\text{Ra} - \text{Ra}_0) / \theta, \quad (4)$

$$\theta = t_0 - 5.555 + \tau / (1 - e^{-\lambda_4 \tau}).$$

These expressions allow the quantity of ionium to be rapidly and exactly estimated without the necessity of

1132 Prof. F. Soddy and Miss A. F. R. Hitchins on the waiting for "transient" equilibrium, that is for $(1 - e^{-\lambda t})$ to become unity.

American Carnotite.

The first mineral to be examined for the ionium-thorium ratio by the above method was American carnotite. A specimen containing some 60 grams of ionium-thorium oxides was sent to us for examination by Mr. W. F. Bleecker, of Boulder, Colorado, U.S.A. It had been separated in his radium factory from hundreds of tons of representative carnotite ore, and from measurements of the rate of growth of radium he had already made it was estimated to contain about 4 per cent. of ionium. In connexion with it he stated that "so far as it is humanly possible for me to tell, no thorium was added to the ionium at any time during its preparation."

A small part of the material was purified from radium by successive precipitations of its solution by ammonia, and then made up to a known weight of solution. One part of this was evaporated and ignited to determine the IoO_2 , ThO_2 content, and the other used for the radium method of estimating the ionium, the weight of IoO_2 , ThO_2 in this part being 75.8 milligrams. The initial radium determined by graphing the results and extrapolating to zero time was 4×10^{-11} gram, and this has been subtracted in the results shown in the following table:—

No. of estimation.	$\text{Ra} - \text{Ra}_0$ ($\times 10^{-11}$ g.).	t_0 (days).	τ (days).	Effective Time θ (days).	Ionium (mg.).
1	3.6	0	1	0.52	2.81
2	9.3	1	1	1.52	2.49
3	17.0	2	0.96	2.51	2.78
4	26.1	3	2	4.06	2.62
5	48.4	5	4	7.24	2.72
6	96.5	9	8	13.93	2.83
7	174.9	17	12	25.01	2.85
8	243.3	29	9	34.67	2.87
Mean					2.75

The quantity of ionium as determined by the mean is 2.75, and by the mean of three final results, which may be regarded as the more trustworthy, 2.85 mg. Accepting the latter figure, the IoO_2 content is 3.23 mg., the percentage of IoO_2 in the oxides 4.26, and the ratio $\text{Io} : \text{Th}$ is 1 to 23.

The Mesothorium-Radium ratio of Radium from Carnotite.— Assuming that no contamination with thorium has occurred during manufacture, it follows that in carnotite there are 23 grams of thorium per gram of ionium or 1.05 kilograms of thorium per gram of radium. McCoy and Henderson (J. Amer. Chem. Soc. xl. p. 1316, 1918) give 19 kilograms as the quantity of thorium in equilibrium with the "milligram of mesothorium," i. e. the quantity of mesothorium which gives a γ -radiation measured through 2 mm. of lead and 1.32 mm. of brass equal to that of a milligram of radium in equilibrium with its γ -ray producing products. Hence per gram of radium separated from American carnotite there must be 0.055 "milligram of mesothorium," or the mesothorium contributes initially one part in 1800 of the γ -radiation. The same authors show that the "milligram of mesothorium," when in equilibrium with radiothorium, gives a total γ -radiation equal to 2.7 mg. of radium. So that as much as 3 parts per 2000 of the γ -radiation of carnotite radium may, as a maximum, be due to thorium products. This is below the error of present methods of γ -ray measurements, and there does not seem to be any valid reason against the use of carnotite radium for standards of measurements.

Joachimsthal Pitchblende.

Being in possession, through the courtesy of the Mines Department of the Government of Czecho-Slovakia, of a set of products from the State radium factory at St. Joachimsthal (now Jachymov, Czecho-Slovakia), upon which much chemical work has been done, it was thought to be of interest to determine the ionium-thorium ratio for this mineral. The method of attack in separating the ionium and actinium from these products was the one now well-established. The behaviour of the ionium and the actinium during the chemical treatments was followed by means of isotopes as indicators, uranium X being used for ionium and mesothorium-2 for actinium, β -ray methods of measurements being employed. Our labours in concentrating the constituents on a large scale were much lightened by a very careful and thorough preliminary examination that had been made of the first product dealt with, by Mr. M. Garrett, who devoted a year to this work.

The material was the "Oxalsäureniederschlag der seltenen Erden," obtained from the first solutions, extracted from the insoluble radium residues of Joachimsthal pitchblende by successive treatments with alkali and acid, by precipitation with oxalic acid. The thorium-ionium ultimately separated, though purified repeatedly by the peroxide method until the

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filtrate failed to give a precipitate on long standing with ammonia, was not completely pure. For on solution in nitric acid temporary discoloration and slight decomposition of the acid occurred. However, this behaviour is observed with thorium preparations containing less than 1 per cent. of impurity, and it is probable that the purity of the material finally separated exceeded 99 per cent. It weighed, as oxide, 44.3 milligrams, and a portion corresponding with 8.9 milligrams of oxide was used for the radium method of estimating the ionium.

No. of estimation.	$Ra - Ra_0$ ($\times 10^{-11}$ g.)	t_0 (days).	r (days).	Effective Time θ (days).	Ionium (mg.).
1	16.2	0.06	2.75	1.55	4.25
2	45.4	2.8	3	4.44	4.16
3	81.6	5.8	4	8.04	4.13
4	128.7	9.8	5	12.67	4.13
5	163.8	14.8	3	16.44	4.06
6	499.6	49	1	49.52	4.12
Mean					4.14

The mean value 4.14 mg. of ionium corresponds with 4.7 mg. of oxide. The proportion of ionium oxide in the preparation is 53 per cent., and the ionium-thorium ratio is 1 : 0.89.

Now this was a very surprising result, because hitherto this ratio has been considered to be 3 : 7, whereas we find actually more ionium than thorium. In 1908, the radium residues from 30,000 kg. of Joachimsthal pitchblende of average uranium content 45 per cent. had been worked up by Haitinger and Ulrich in the chemical factory of the Austrian Gasglühlicht und Elektrizitätsgesellschaft. Out of the rare-earth fraction, A. v. Welsbach, in 1910, separated a few grams of pure ionium-thorium oxide, upon which most of the subsequent work has been performed. From the atomic weight, 231.51, obtained by Hönigschmid and Horowitz in 1916, regarded as a mean between that of thorium 232.12 and of ionium 230, the ionium-thorium ratio works out as 3 : 7. Stefan Meyer, comparing the α -radiation of this preparation with that of radium, found, allowing for the slight difference in the ranges of the α -particles, that one gram of the former emitted as many α -particles as 5.07 milligrams of radium, and from this calculated the period of ionium as 1.4×10^5 years, when that of radium is 2400 years*.

If we recalculate our result by formula (4) substituting 1.4×10^5 for 1.1×10^5 for $1/\lambda_2$, there would be 5.27 mg. Io, = 6.0 mg. of IoO_2 , in the 8.9 mg. of oxides, or 67.4 per cent.,

* Compare Ann. Rep. Chem. Soc. 1916, p. 251; Stefan Meyer, *Sitzungsber. k. Akad. Wiss. Wien, II. a.*, cxxv. p. 191 (1916).

and the ionium-thorium ratio would be practically 2 : 1. Or, conversely, if we calculate the period of ionium from our result for the rate of formation of radium, assuming that the material is 30 per cent. ionium, the result is 7×10^4 years. So that it did not seem possible that the ionium-thorium ratio in Joachimsthal pitchblende could be as low as that hitherto accepted.

In order to check the result, another of the products from the State factory at St. Joachimsthal was worked up for ionium and actinium. This product was the "Sodaniederschlag." So far as we are aware it has not previously been chemically examined, although, from our present knowledge of the chemistry of the radio-elements, it is to be expected to contain actinium and ionium in notable amount. It is derived, not from the radium residue, which is the part of the mineral insoluble in sulphuric acid, but from the uranium solution, during purification of the uranium, as a precipitate when the solution is treated with sodium carbonate, the uranium remaining dissolved.

The ionium-thorium oxides separated from these residues weighed 19.7 mg., and a part equivalent to 3.9 milligrams was used for the radium estimation of ionium. Both in this and the preceding case no initial radium was present.

No. of estimation.	Ra—Ra ₀ ($\times 10^{-11}$ g.).	t_0 (days).	τ (days).	Effective Time θ (days).	Ionium (mg.).
1	10.5	0.17	3.75	2.26	1.89
2	24.4	4	3	5.64	1.77
3	37.8	7	3	8.64	1.78
4	51.6	10	4	12.24	1.72
5	147.6	33	1	33.52	1.79
Mean					1.79

1.79 mg. of ionium correspond with 2.05 mg. of oxide and the proportion of ionium oxide in the preparation is 52.5 per cent. The ionium-thorium ratio is as 1 : 0.9, substantially the same as before. Thus the very high proportion of ionium in the material is confirmed for another and different product of the same material.

The Mesothorium-Radium ratio for Radium from Joachimsthal pitchblende.—Accepting the ionium-thorium ratio as 1 : 0.9, and the period of ionium as 1.1×10^5 years, per gram of radium in the pitchblende there are 46 grams of ionium and 41 grams of thorium, a total of 87 grams of thorium isotopes. Or, per 1000 kg. of uranium ($= 0.34$ g. radium) there are respectively 15.6, and 14, with a total of 29.6 grams. The "milligram of mesothorium" is initially present in 450 grams of the radium from this mineral, so that one part

in 450,000 of the γ -radiation is due to mesothorium, or, including the radiothorium, 6 parts in a million, as a maximum, is due to thorium products. This is, of course, of no significance as regards the constancy of the γ -rays, though it may be easily put into evidence by chemical methods ('Nature,' xci. p. 934, 1913).

The recent results of Meyer and Ulrich.

Since the work described was completed, our attention has been directed to a recent paper by Meyer and Ulrich (*Sitzungsber. Akad. Wiss. Wien*, II. a, cxxxii. p. 279, 1923), in which some of our results have been anticipated. They have examined the ionium-thorium content of Joachimsthal pitchblende to ascertain whether specimens from different quantities of the material had the same composition, particularly from the point of view of a suggestion of G. Kirsch *, that an isotope of uranium of atomic weight 236, and period about 10^8 years, may be the first member of the thorium disintegration series, and that thorium may be the product of this in an α -ray change. In this event, if Joachimsthal pitchblende were a mineral of recent formation, different specimens of different age might show different ionium-thorium content.

Meyer and Ulrich have prepared two new thorium-ionium preparations from the rare-earths, separated in various stages of the manufacturing process, from the mineral worked up in the State factory at St. Joachimsthal in 1912 and 1913. The first of these only is as yet sufficiently free from the isotopic radioactinium to allow of an exact α ray comparison with the preparation for which the atomic weight 231.51 was found. The new preparation was found to be more active in the ratio 100 : 60, and the authors conclude that if the latter is 30 per cent. ionium, the new preparation must consist of very nearly equal quantities of ionium and thorium, and should possess an atomic weight of 231.1. This result is thus precisely what we have found, although the methods of estimating the ionium are totally different, and, as has been shown, not entirely consistent. The authors conclude that their results make it certain that the ionium-thorium mixture from different samples of Joachimsthal pitchblende must vary between 30 and 50 per cent., and they discuss this in connexion with the supposed parent of thorium.

In our view, however, the probable explanation is not so far to seek. Since we have found essentially the same 1 : 1 ionium-thorium ratio as Meyer and Ulrich, the natural conclusion is that the preparation separated by Welsbach, for

* G. Kirsch, *Sitzungsber. Akad. Wiss. Wien*, II. a, cxxxi. p. 551 (1922).

which a 3:7 ratio was found, is exceptional, and has probably been contaminated by extraneous thorium. It was worked up in 1908, before anything was known about isotopes, by Haitinger and Ulrich in a thorium factory, and the dust settling from the air, without any more direct contamination, might well account for the difference, even before the ten tons of raw material found its way into Welsbach's hands. The subsequent separation of the ionium occupied two years, and presumably, though the fact is not explicitly on record, this further working up took place also in a thorium factory. Indeed it must be considered remarkable that the contamination was not greater, and the 3:7 ratio must be rather regarded as eloquent of the great cleanliness and care with which this, then extraordinarily complicated and difficult operation, was conducted.

Summary.

1. Recent redeterminations of the average-life period of ionium, from the rate of growth of radium in four uranium preparations purified from 18 to 15 years ago, give for the mean value 1.08×10^5 years. This is 8 per cent. higher than the value arrived at in 1919, and it is suggested that the rounded value 1.1×10^5 years should be meantime adopted.

2. An exact method is described for the determination of ionium, assuming this period from the rate of growth of radium, and which is applicable to very active preparations. The "effective time" of accumulation, θ , is given by

$$\theta = t_0 - 5.555 + \tau / (1 - e^{-\lambda_4 \tau}),$$

where t_0 is the time from purification to sealing the preparation, τ the time of accumulation of emanation, and λ_4 the radioactive constant of the latter, in days. Then

$$I_0 = 4.08 \times 10^7 (Ra - Ra_0) / \theta,$$

where $Ra - Ra_0$ is the radium produced by the quantity I_0 of ionium (grms.).

3. An examination of an ionium-thorium mixture separated from many hundreds of tons of representative American carnotite, gave the ionium-thorium ratio as 1:23. Radium prepared from this source will have as a maximum 3 parts per 2000 of the γ -radiation contributed by mesothorium and radiothorium.

4. Two specimens of ionium-thorium have been separated from different products of the working up of the Joachimsthal pitchblende, the first from the oxalic acid precipitate, containing rare-earths, separated from the insoluble radium

residues, and the second from the sodium carbonate precipitate from the solution of the mineral in sulphuric acid, in the uranium purification. Both specimens showed that the ionium-thorium ratio was 1:0.9, the ionium actually predominating.

5. Results recently published by Meyer and Ulrich on a thorium-ionium preparation separated from the rare-earths in the material worked up in St. Joachimsthal in 1912 and 1913, give an α -radiation greater than that prepared by Haitinger and Ulrich and A. v. Welsbach in 1908-1910, for which the atomic weight 231.51 and the ionium-thorium ratio 3:7 have been accepted. This is in agreement with our result that the quantities of ionium and thorium in the mineral are nearly equal. We suggest that the older preparation was contaminated through having been worked up in a thorium factory.

We wish to express our acknowledgements to Mr. Bleecker of Boulder, Colorado, and to the Department of Mines of Czecho-Slovakia, for the materials examined, and to Mr. M. Garrett, Rhodes Scholar of Exeter College, for valuable assistance in chemical investigations preliminary to this work.

Old Chemistry Department,
University Museum, Oxford,
April 19th, 1924.

CXI. *Note on the Relativity Dynamics of a Particle.*

By P. A. M. DIRAC, *St. John's College, Cambridge* *.

A VELOCITY corresponds to a direction in four-dimensional space-time, and is determined by the ratios of the components of a vector drawn in that direction. The velocity of matter may be defined in two ways. If we can identify and follow the motion of a particular particle or other discontinuity, the direction of its world-line gives us the "kinematical velocity." Alternatively, if we measure the three components of momentum-density and the mass-density at any point, then in certain cases (which include that of an isolated particle) the direction determined by the four quantities is invariant, and it then gives the "dynamical velocity." In Eddington's derivation of the gravitational equations †, mass and momentum are defined through their property of conservation without reference to the conception

* Communicated by Prof. A. S. Eddington, F.R.S.

† 'The Mathematical Theory of Relativity,' Ch. iv.

of kinematical velocity, so that the identity of the two definitions is not immediately obvious. Eddington has proved the identity of the definitions for an isolated particle when it has three perpendicular planes of symmetry^{*}; but it can be done without any postulates concerning the form of the particle, by considering the conditions that hold at surfaces of discontinuity in a distribution of matter.

The simplest case in which kinematical velocity has a meaning is that of a (three-dimensional) surface of discontinuity separating a region containing a continuous distribution of matter from a region containing none; in that case the normal component of the kinematical velocity of the matter at the surface is zero in any system of coordinates for which the equation of the surface does not involve x_4 . We choose our system of coordinates such that the equation of the surface is $x_1 = \text{constant}$. Since the divergence of the material energy-tensor vanishes, we have in the usual notation

$$\frac{\partial T^{\mu\nu}}{\partial x_\nu} + \{\alpha^\nu, \mu\} T^{\alpha\nu} + \{\beta_\nu, \nu\} T^{\mu\beta} = 0,$$

which may be written

$$\frac{\partial T^{\mu 1}}{\partial x_1} = -\frac{\partial T^{\mu 2}}{\partial x_2} - \frac{\partial T^{\mu 3}}{\partial x_3} + \frac{\partial T^{\mu 4}}{\partial x_4} - \{\alpha^\nu, \mu\} T^{\alpha\nu} - \{\beta_\nu, \nu\} T^{\mu\beta}.$$

The terms on the right are all finite at the boundary, however rapid the transition from finite density to zero density may be. Hence $\frac{\partial T^{\mu 1}}{\partial x_1}$ is also finite at the boundary, so that $T^{\mu 1}$ is continuous, and therefore vanishes just inside the region containing the matter. So the normal component of the dynamical velocity of the matter at the boundary vanishes, in agreement with all that is known concerning the kinematical velocity.

We now consider a particle in free space, whose equations may be taken to be $x_1 = \text{constant}$, $x_2 = \text{constant}$, $x_3 = \text{constant}$, so that its kinematical velocity vanishes in these coordinates. Then $T^{\mu 1}$, $T^{\mu 2}$, and $T^{\mu 3}$ are continuous at the surface of the tube which is occupied by the particle, and therefore vanish inside it. We are here assuming that the differences in $T^{\mu\nu}$ at different points of a section of the tube are negligible, this being what is meant by a simple particle. So all the components of $T^{\mu\nu}$ vanish except T^{44} , and the dynamical velocity is zero. Hence the dynamical velocity vector has the same direction as the kinematical velocity vector, viz. along x_4 .

^{*} *Loc. cit.* § 56.

CXII. *Notices respecting New Books.*

An Introduction to the Theory of Optics. By Sir ARTHUR SCHUSTER, Sc.D., F.R.S., &c. Third Edition, revised and enlarged by the Author and J.W. NICHOLSON, M.A., D.Sc., F.R.S. (Pp. xv + 397, with 188 figures.) (London : Edward Arnold & Co., 1924. Price 18s. net.)

A Treatise on Light. By R. A. HOUSTOUN, M.A., Ph.D., D.Sc., Lecturer on Physical Optics in the University of Glasgow. Fourth Edition. (Pp. x + 486, with 334 figures and 2 plates.) (London : Longmans, Green & Co., 1924. Price 12s. 6d. net.)

BOTH of these well-known works on optics have passed into new editions. The previous editions of Schuster's work appeared in 1904 and 1909 respectively, whilst those of Houston's appeared in 1915, 1921, and 1923. The additions and changes in the new editions are in both instances comparatively slight and therefore detailed comment is not necessary.

The most important addition to the 'Theory of Optics' consists of the addition of two new chapters entitled "Emission Spectra and the Quantum Theory" and "Dynamical Theory of Spectra" respectively. These are presumably by Prof. Nicholson, an acknowledged authority on the subjects in question. The volume will long continue to remain the best introduction from the physical standpoint to the theory of optics. On account of its originality of treatment and the clearness and precision of the English it should be carefully read by every serious student of the subject. A word of praise is due to the publishers for the excellence of the printing.

The new matter in the latest edition of Houston's work consists of a very brief chapter on recent advances, a new index, and two coloured plates. The scope of this volume, which is intended for students who have completed a first year's course in physics and are proceeding further with the study of light, is a very comprehensive one. It is divided into four parts, dealing respectively with Geometrical Optics, Physical Optics, Spectroscopy and Photometry, and the Mathematical Theory. A student who has mastered this book will be well equipped for the more detailed study of any special portion of the subject. The author's considerable experience in teaching has enabled him to smooth out the difficulties which the student is likely to encounter and to present the subject in the simplest manner. The chapter dealing with systems of lenses may be mentioned as an example of simplicity of treatment. That a fourth edition is now required is proof that the volume has met a real need. The paper and printing could be improved upon but, on the other hand, the price has been kept to a reasonable figure, an important consideration for a volume which is designed as a student's textbook.

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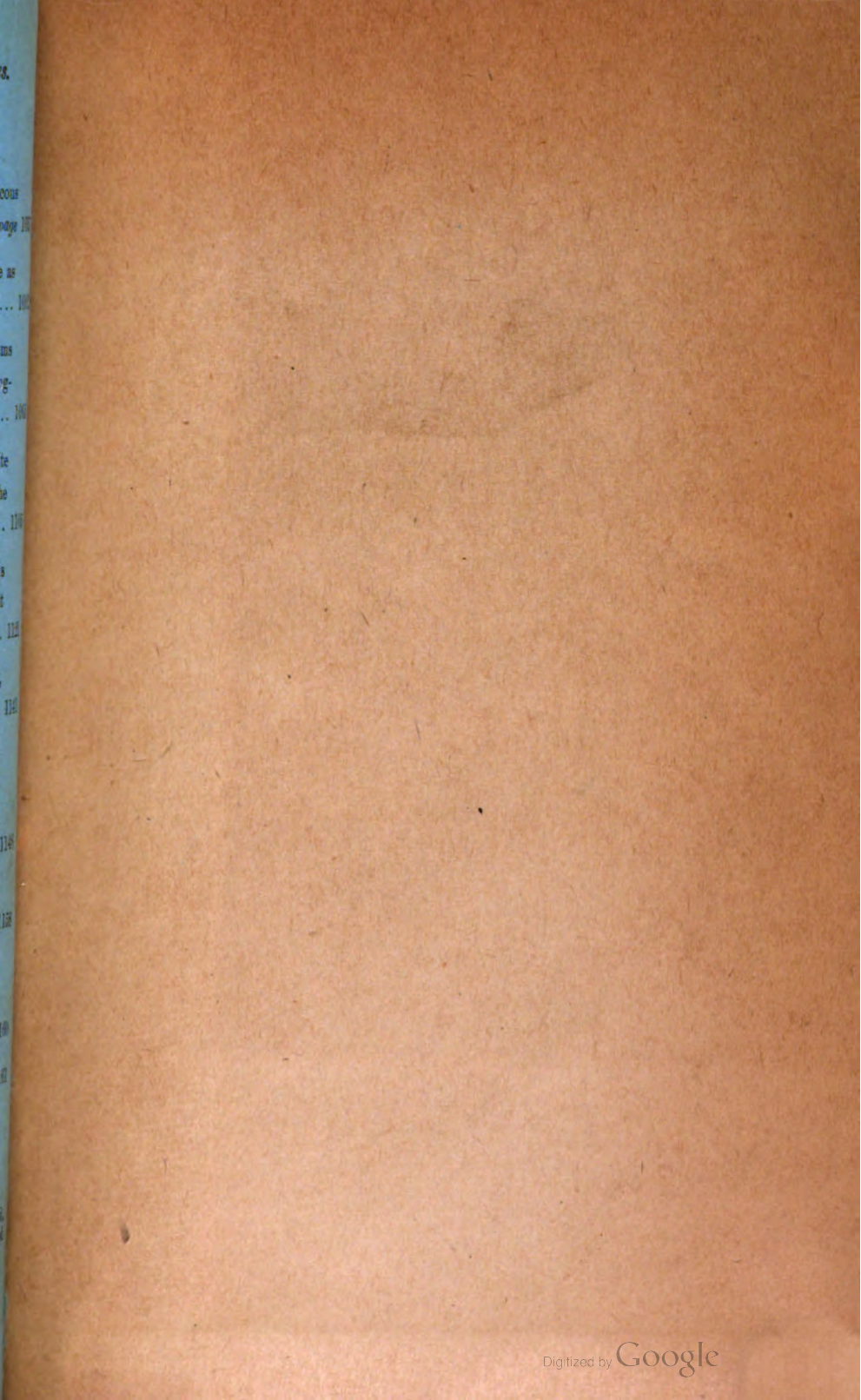
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